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INTERPRETATION OF RATE DATA FOR MULTIPLE-STEP
CHEMICAL REACTION SYSTEMS

BY



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A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES IN
PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE
DEGREE OF MASTER OF SCIENCE IN
CHEMICAL ENGINEERING

DEPARTMENT OF CHEMICAL AND PETROLEUM ENGINEERING

EDMONTON, ALBERTA

FALL, 1970

Thesis
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UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance a thesis entitled "INTERPRETATION OF RATE DATA FOR MULTIPLE-STEP CHEMICAL REACTION SYSTEMS" submitted by Aung Myint in partial fulfilment of the requirements for the degree of Master of Science in Chemical Engineering.

Abstract

A numerical method for interpreting experimental kinetic data from multiple-step chemical reaction systems was developed. The procedure involves transforming the rate data obtained for each participating chemical component into rate data for each reaction step involved in the overall system. The sets of data for each single reaction step may then be used to construct an overall kinetic model which is consistent with the observed chemistry and order of reaction exhibited by each of the various components participating in the various reaction steps. The procedure may be used with either concentration-time or differential rate data taken under isothermal conditions.

The method is developed by using simulated kinetic data containing normally distributed random error. It is then applied to two sets of experimental rate data obtained from the literature. The applicability and accuracy of the proposed technique are believed to be at least comparable, if not superior, to other nonlinear estimation methods currently available.

ACKNOWLEDGEMENTS

The author wishes to acknowledge his sincere gratitude to Dr. I.G. Dalla Lana, Department of Chemical and Petroleum Engineering, University of Alberta, for his guidance and supervision during the course of this project.

The financial support received from the National Research Council of Canada is gratefully acknowledged.

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CHAPTER I

INTRODUCTION AND LITERATURE SURVEY

1.1. Introduction

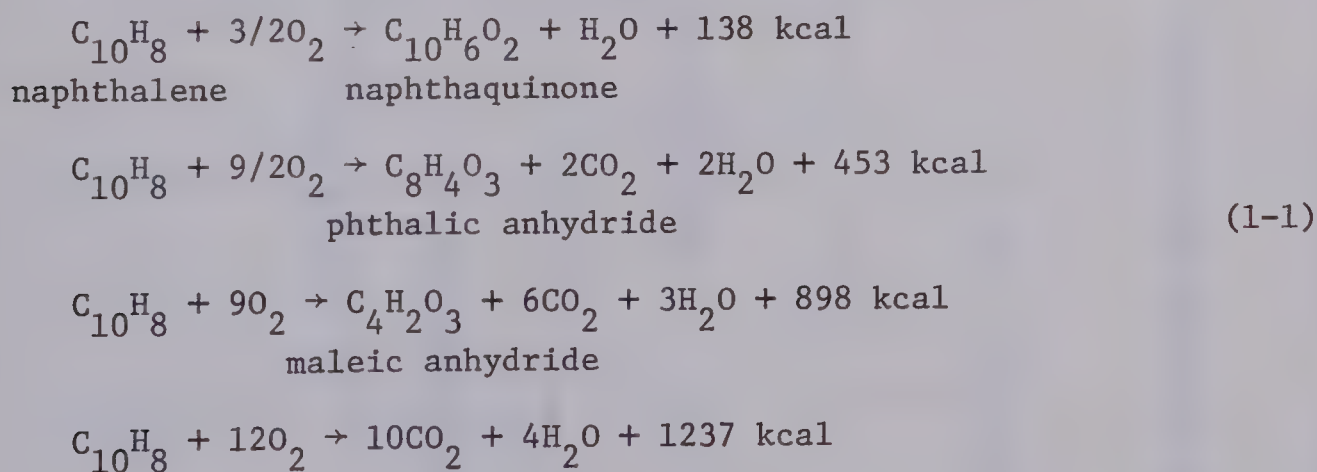
Many chemical reactions occurring in nature or in the laboratory do not exhibit a single elementary step between reactant molecules but follow a mechanism which involves several such elementary reaction steps in various combinations of series and parallel forms. In the laboratory, one of the most common methods used to study the behavior of a reaction is to obtain the composition data of the reacting components as a function of reaction time. For these experimental data to be useful in analysis, future experimental design or simulation, a kinetic model describing the apparent chemical reaction steps, and the associated parameters (here parameter is used for both rate constant and order of reaction) must be determined but consistent with the experimental data. In view of the modelling and computational problems encountered in the analysis of multiple-step chemical reaction systems: the complexity of the chemistry, the various combinations of parallel and consecutive multiple reaction steps possible, and the uncertainty in the reaction order associated with each reacting component, an approach would be desirable in which a kinetic model may be determined from experimental data, and at the same time, the conventional trial-and-error procedure may be eliminated. Some representative multiple-step chemical reaction system from recent literature can be described as follow.

1.1.1. Dehydrogenation of N-propanol

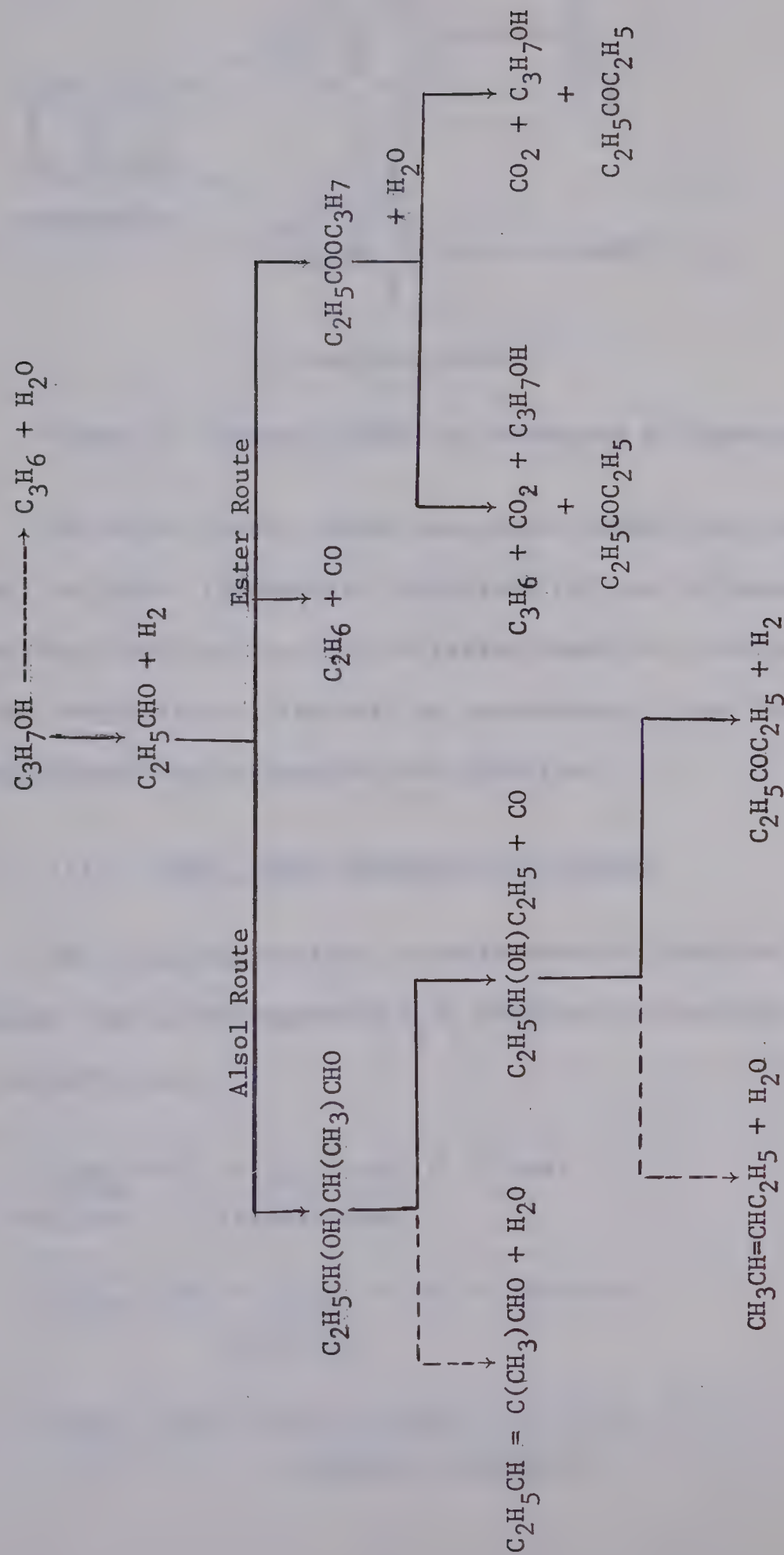
Wanke [37] has studied the reaction of dehydration and dehydrogenation of n-propanol on NaOH treated Alundum catalyst at a reaction temperature of 463°C and space time ranging from 0 to 150 (hr-gm of cat./gm-moles of feed). The reaction scheme is shown in Figure 1. It exhibits a concurrent reaction step of dehydration and dehydrogenation of n-propanol, and subsequently from propionaldehyde, two alternative paths, the aldol route and ester route, are branched. From the aldol route, through the intermediate product of 3-pentanol, and also from the ester route by hydrolysis, diethyl ketone is formed.

1.1.2. Vapor phase catalytic oxidation of naphthalene

Ioffe and Sherman [18] have studied the vapor phase catalytic air oxidation of naphthalene over V_2O_5 catalyst at reaction temperature ranging from 240° to 400°C. The stoichiometry for the exothermic reactions which form the various products can be described as below:



From the reaction system as shown in equation (1-1), and the results obtained from their experiments, they have proposed a kinetic model as shown in Figure 2.



Solid lines represent main reaction steps while dashed lines stand for side reaction steps.

Figure 1. Reaction Model for Dehydrogenation of N-propanol

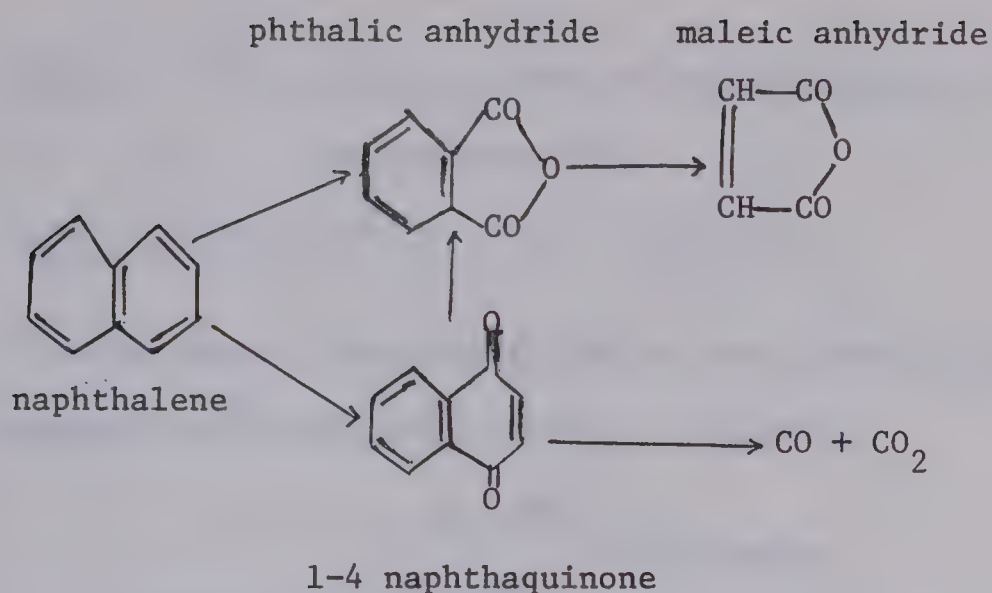
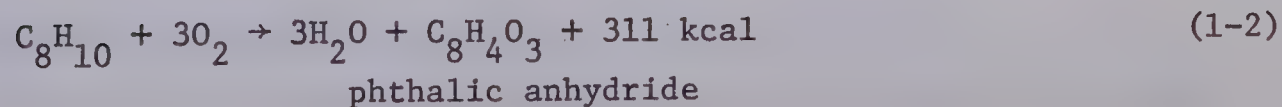
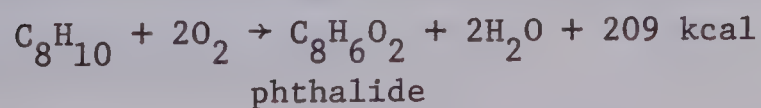
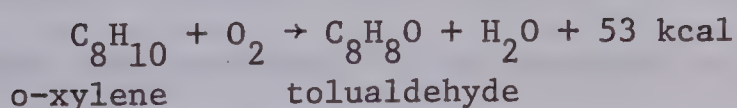


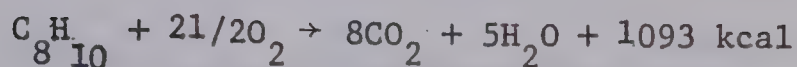
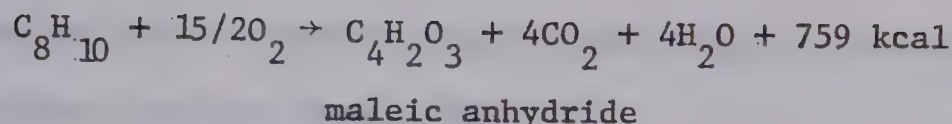
Figure 2 Chemical Model for Oxidation of Naphthalene

The above kinetic model involves a closed loop series of reaction steps, and since the analytic solutions for the differential equations describing the kinetics of this system cannot be obtained explicitly a priori, more difficulties will be encountered if one tries to use some methods involving integrated rate equations.

1.1.3. Vapor Phase Oxidation of O-Xylene

The equations written in stoichiometric form for oxidation of o-xylene over a SiC-supported V_2O_5 catalyst at reaction temperatures from 400 to 450°C are





Simard, Steger, and Arnott [35] in their study of this system have proposed the kinetic model shown in Figure 3.

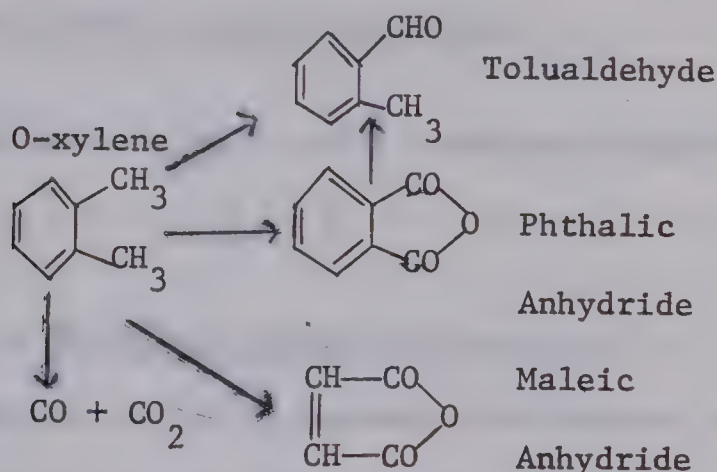


Figure 3 Chemical Model for Oxidation of O-xylene

The same difficulty as described in section (1.1.3.) will be encountered in analyzing the kinetic model shown in Figure 3.

Before one proceeds to classify various methods of estimating parameters of a given kinetic model for a multiple-reaction system such as those just described, it is necessary to review briefly the conventional methods of handling single step reactions, and the accuracy of the parameters thus obtained.

1.2. Methods of evaluating single-step reaction parameters

The majority of methods for estimating rate constants and order

Mathematics

Chapter 1: Introduction

Mathematics is the study of quantity, structure, and change.

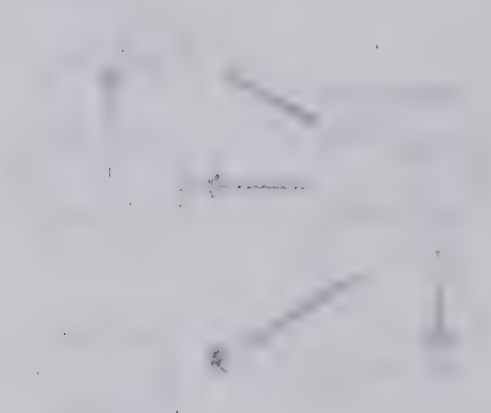
It is a universal language that describes the world around us.

Definition:

Example:

Exercise:

Conclusion:



Chapter 2: Algebra

Algebra is the study of mathematical symbols and the rules for manipulating these symbols.

It is a branch of mathematics that deals with the properties and manipulation of symbols.

Algebra is a fundamental tool for understanding the world around us.

It is a branch of mathematics that deals with the properties and manipulation of symbols.

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It is a branch of mathematics that deals with the properties and manipulation of symbols.

Chapter 3: Geometry

Geometry is the study of shapes, sizes, and positions of objects.

of reaction for a reaction system involving only a single step, can be classified into four categories:

1.2.1. Method of integrated equation

1.2.2. Method of differentiation

1.2.3. Method of half-life times

1.2.4. Other special techniques

These methods will now be examined briefly in the following sections:

1.2.1. Method of integrated equation

A reaction order is assumed with respect to each reactant and the differential form of the rate equation is then integrated to give a relation between the concentration and the corresponding reaction time.

Take a reaction of the type, $2A \rightarrow \text{products}$, which follows a second-order rate equation, as an example, using the nomenclature of page 122,

$$-\frac{d C_A}{d t} = k C_A^2 \quad (1-3)$$

Upon integration from $t=0$ to $t=t$ and corresponding $C_A=C_{A0}$ and $C_A=C_A$, one obtains

$$\frac{1}{C_A} - \frac{1}{C_{A0}} = kt \quad (1-4)$$

The adequacy of the integrated equation in fitting the experimental rate data may be tested graphically by the linear plot of $1/C_A$

against time. Laidler [21] points out that the integration method characterizes a reaction according to the way in which the concentration of a product or a reactant varies with the time, and this may give rise to misleading deductions about the way in which the rate varies with the concentration of the reactants.

1.2.2. Method of differentiation

In this method, values for the left-hand-side of the differential form of rate equation, $\frac{dC_A}{dt}$, are obtained by graphically or numerically differentiating the concentration-time data. On taking logarithms of both sides of equation (1-3) one obtains,

$$-\log[dC_A/dt] = \log k + 2\log C_A \quad (1-5)$$

The slope or the intercept obtained by plotting the logarithm of rate vs. logarithm of concentration, or by plotting dC_A/dt , versus C_A^2 will directly give the rate constant.

Using the procedure summarized by Walas [36] of plotting the data by hand and then using optical methods to fit functions to the data, often unintentionally biased as well as tedious, it is difficult to obtain rate data sufficiently precise to establish the reaction order correctly. Also, because of the scattering of the data due to experimental error, considerable further uncertainty may be introduced by the process of numerical differentiation using the conventional 3-point or 5-point difference formulae.

This weakness will be shown in detail in chapter 3.

1.2.3. Method of half-life times

The half-life of a reactant; the time required for one-half of a given reactant ($x=0.5C_{A0}$) to be consumed, is also an useful approach. For a second-order reaction, integration of equation (1-3), between the limits, $t=0, C_A=C_{A0}$ and $t=t, C_A=0.5C_{A0}$, gives

$$t_{1/2} = 1/kC_{A0} \quad (1-6)$$

The rate constant can be obtained from the measurements of half-life for different initial concentrations. Equivalent techniques are used for other orders as well.

1.2.4. Method of reference curves

Walas [36] suggests a method of estimating the reaction order without finding the rate constant. Here, a reference plot of ratio of the time required to reach any conversion by the time required to reach 90% conversion versus per cent conversion is provided. The data are plotted on the same scale and on the reference plot, which consists of a family of curves corresponding to various orders. The order of reaction is estimated by selecting the member of the family of curves which fits most satisfactorily.

Very often, this method becomes impractical, because of the requirement of large values of conversion, such as 90%. Moreover since the family of curves on the reference plot are limited, only an approximate value of reaction order can be obtained.

As outlined, even for simple reaction systems the analysis for determining reaction order and rate constant is very cumbersome by using the method of integrated equation when the order of reaction is unknown. Although the method of differentiation appears to be more promising, this is true only when the accuracy of the rate data obtained by numerical differentiation of composition-time data is within experimental error. Thus, for complex reaction systems involving various combinations of single-step reactions in series and/or parallel form and cyclic or close loop combinations abundant problems may be expected.

During the last decade, a considerable amount of work in the area of estimation of rate constants for a given kinetic model for a multiple-step reaction system has been done [4,16]

Before one proceeds to classify the various methods, it is desirable to clarify the conditions under which the reaction occurs, the mathematical representation of a multiple-step reaction system, and finally the method of non-linear least squares.

1.3. Reaction conditions

The hypothetical kinetic model which will be presented to demonstrate the applicability of this work in chapter 4 and all other cases, except where stated otherwise, will be assumed to occur isothermally in a constant volume perfectly mixed reactor. Since the analysis of the rate data obtained under these experimental conditions does not discriminate between chemical or physical rate-controlling influences, to all practical purposes then, the reaction systems are treated as though they were homogeneous ones.

1.4. Mathematical model for a complex reaction system

For an m-component multiple-step reaction system, the rate of each reacting component can be mathematically expressed as:

$$\begin{aligned}
 \frac{dC_1}{dt} &= r_{11}(C_1, \dots, C_m) + \dots + r_{1j}(C_1, \dots, C_m) + \dots + r_{1n}(C_1, \dots, C_m) \\
 &\cdot \\
 &\cdot \\
 \frac{dC_i}{dt} &= r_{i1}(C_1, \dots, C_m) + \dots + r_{ij}(C_1, \dots, C_m) + \dots + r_{in}(C_1, \dots, C_m) \\
 &\cdot \\
 &\cdot \\
 \frac{dC_m}{dt} &= r_{m1}(C_1, \dots, C_m) + \dots + r_{mj}(C_1, \dots, C_m) + \dots + r_{mn}(C_1, \dots, C_m)
 \end{aligned}
 \tag{1-7}$$

where the terms, $r_{ij}(C_1, \dots, C_m)$, denote any general concentration-dependent function.

In compact form, one can rewrite the set of equations by

$$\frac{dC_i}{dt} = \sum_{j=1}^n r_{ij}(C_1, \dots, C_m) \quad (1-8)$$

The rate of reaction for a system which fulfils the reaction conditions described in section (1.4), can be expressed as :

$$r_{ij} = k_j f_{ij} \quad (1-9)$$

Therefore,

$$\frac{dC_i}{dt} = \sum_{j=1}^n k_j f_{ij} \quad (1-10)$$

1.5. Method of linear least squares

The method of linear least squares which is used as a criterion for estimating the rate constants for a multiple-step kinetic model can be summarized as follow. Integrating the differential equation (1-10), which represents the rate of each reacting component, from $t=t_0$, to $t=t_u$, one obtains,

$$C_i(t_u) - C_i(t_0) = \sum_{j=1}^n k_j \int_{t_0}^{t_u} f_{ij} dt \quad (1-11)$$

If Y_{iu} is used to denote predicted values of $[C_i(t_u) - C_i(t_0)]$, and \hat{Y}_{iu} represents the experimental values, then the rate constants k_j can be estimated by minimizing D which is the sum of the squares of the difference, $(Y_{iu} - \hat{Y}_{iu})$.

Mathematically D can be written as follow:

$$D = \sum_{u=1}^Q \sum_{i=1}^m [Y_{iu} - \hat{Y}_{iu}]^2 \quad (1-12)$$

Since that D is unconstrained it may be minimized by equating

$\partial D / \partial k_j = 0$, then equation (1-12) becomes

$$2 \sum_{u=1}^Q \sum_{i=1}^m [(Y_{iu} - \hat{Y}_{iu}) \partial Y_{iu} / \partial k_j] = 0 \quad (1-13)$$

By employing equation (1-13), rate constants k_j can be estimated for a set of experimental data.

Now, the various methods of estimating rate constants for multi-step kinetic models may be classified as follow:

1.6. Methods of evaluating rate constants for multi-step kinetic models

The methods of estimating rate constants for multi-step kinetic models can be generally classified into six categories as follow:

1.6.1. Analytic integration of differential equations, followed by non-linear least squares regression to obtain values of the rate constants.

1.6.2. Numerical integration of differential equations, followed by non-linear least squares regression.

1.6.3. Differentiation of experimental data followed by linear least squares regression.

1.6.4. Simulation on an analog computer and trial-and-error scaling of parameters

1.6.5. Approximate solutions developed for specific chemical reaction systems.

1.6.6. Elimination of time variable from the differential rate equations.

1.6.7. Quasilinearization.

Now, the various methods listed in section (1.3) will be examined briefly as follow:

1.6.1. Analytic integration followed by non-linear least squares regression

The integration of the differential form, of rate equation performed in this method is equivalent to the method of integration for single-step reaction system described previously in section (1.2.1.). The order of reaction with respect to each reacting component must be assumed a priori. Subsequently the rate constants are estimated by using equation (1-13).

This method may work successfully, even with an approximation, with systems involving sets of ordinary differential rate equations such as those obtained for simple reaction mechanisms. But more often it is not a suitable method since most realistic models are not simple ones.

1.6.2. Numerical integration, followed by non-linear least squares regression

In this method, the integration step is no longer limited to forms of ordinary differential equations for which analytic solutions are available, consequently, the order of reaction can be either a fractional number or an integer.

The partial derivatives of Y_{iu} with respect to k_j in equation (1-13) can be expanded as below:

$$\frac{\partial Y_{iu}}{\partial k_j} = \frac{\partial \left[\sum_{j=1}^n k_j \int_{t_0}^{t_u} f_{ij} dt \right]}{\partial k_j}$$

$$\frac{\partial Y_{iu}}{\partial k_j} = \int_{t_0}^{t_u} f_{ij} dt + \sum_{j=1}^n k_j \int_{t_0}^{t_u} \frac{\partial f_{ij}}{\partial k_j} dt \quad (1-14)$$

Himmelblau et al. [16] and Ball et al. [4] have ignored each high partial derivative term under the assumption of small contribution by $\frac{\partial f_{ij}}{\partial k_j}$. Thus, equation (1-13) reduces to

$$\sum_{u=1}^Q \sum_{i=1}^m 2 \left\{ \left[\sum_{j=1}^n k_j \int_{t_0}^{t_u} f_{ij} dt - \hat{Y}_{iu} \right] \times \left[\int_{t_0}^{t_u} f_{ij} dt \right] \right\} = 0 \quad (1-15)$$

Himmelblau and his co-workers have assumed the functional relationship, f_{ij} , between time and concentration during integration. Ball et al. have applied their procedure in a similar way to a reaction system of five components in which each of the reaction steps follow second-order kinetics. To reduce the computations required, they suggested that integration of only three differential equations be carried out for their reaction system, the remaining two unknowns can be computed from two independent material balance relations based on the original composition.

Later, Hunter [17] has shown that for the least squares criterion to give the maximum likelihood estimates of the required parameters from multiresponse data, normally distributed data, equal error variances for all responses, and absence of error covariance between any two responses were required.

Eakman [12] claimed that these restrictions cannot be generally applied to kinetic data. With the rate constants estimated from equation (1-15), he has introduced an additional step involving the hill-climbing

method to minimize the determinant criterion. This criterion has been derived by Box and Draper [6], and may be expressed as:

$$\Delta = \begin{vmatrix} S_{11} & S_{12} & \cdot & \cdot & \cdot & \cdot & S_{1n} \\ S_{21} & S_{22} & \cdot & \cdot & \cdot & \cdot & S_{2n} \\ \cdot & & & & & & \\ \cdot & & & & & & \\ \cdot & & & & & & \\ \cdot & & & & & & \\ S_{n1} & S_{n2} & \cdot & \cdot & \cdot & \cdot & S_{nn} \end{vmatrix} \quad (1-16)$$

The terms which make up this determinant are

$$S_{ii} = \sum_{u=1}^Q [C_i(t_o) - C_i(t_u) + \sum_{j=1}^n k_j \int_{t_o}^{t_u} f_{ij} dt]^2 \quad (1-17)$$

on the main diagonal and

$$S_{mi} = S_{im} = \sum_{u=1}^Q [C_i(t_o) - C_i(t_u) + \sum_{j=1}^n k_j \int_{t_o}^{t_u} f_{ij} dt] \times [C_m(t_o) - C_m(t_u) + \sum_{j=1}^n k_j \int_{t_o}^{t_u} f_{mj} dt] \quad (1-18)$$

in other positions. Using this criterion, the only condition required is normal distributed error around the true value. With a given kinetic model, the method estimates the rate constants effectively. But with kinetic models in which the order of reaction is unknown, the procedure is still cumbersome.

In the case of complex reaction systems following first-order kinetics, Wei and Prater [39] have treated this class of problem rigorously and in detail. They showed how the linear first-order ordinary differential equations (coupling variables, in the case of reversible or

cyclic reaction system) can be transformed to an equivalent set of equation describing a hypothetical system, each equation of which contains only one dependent variable. The equivalent set may then be solved by standard matrix algebraic methods to give the usual exponential type of integral equation as the solution. With this matrix transformation, they successfully reduce problems of the class in section (1.6.2.) to the ones in section (1.6.1.).

In this method, to perform the transformation, the square matrix K of unknown rate constants must be used and consequently, an iterative calculation procedure is required. In spite of its many elegant features, the Wei and Prater method is limited to first-order kinetic models.

When multiple-step reactions can be approximated by a first-order model they may be handled by their method, but very often this approximation is satisfied only for a limited region of the experimental conditions. Ames [1], Aris [2], and Wei [38] have independently shown how a non-linear reaction system can be reduced to a linear one, and thereby the system in the linear form can be handled by Wei and Prater method. But the mathematics of transformation is rather complicated and the method is still limited to system exhibiting simple non-linear kinetic behavior.

1.6.3. Direct differentiation of composition-time data

Levenspiel [24] describes the common graphical procedure showing how the reaction rates for a set of concentration-time data, can be obtained. The procedure involves smoothing the experimental data points first by drawing smooth line through them and then tangents were drawn

at several points on the smooth curve corresponding to different time intervals. Subsequently, linear least squares regression was applied to the rate and corresponding concentration data. If the order of reaction is other than first order, a logarithmic transformation procedure, as described previously in method of differentiation for simple reaction, was applied. In this way, rate constant and order of reaction can be estimated at the same time.

Because the method of smoothing of the experimental data which was used and the graphical method of differentiation is generally influenced by the experimenter's biases, the results can occasionally be misleading or ambiguous. Its outstanding feature is of course that rate constant and order of reaction can be obtained simultaneously.

Bak [3] recommends a procedure for smoothing the experimental data, measured at equidistant values of time, using third order orthogonal polynomials to approximate the data by minimizing the sum of the squares of the differences between the predict values and the experimental data values. He then proposed to replace the experimental data points by the corresponding values of the approximated polynomials. The reaction rate is obtained by differentiating the polynomials. Subsequently, rate constants can be approximated by applying linear least squares to fit the data.

Lindsay [25] observed that one of the reasons why the reaction rate, $\frac{dC_A}{dt}$, cannot be obtained precisely is due to the variation in magnitude of $\frac{dC_A}{dt}$ over the course of an experiment, i.e., the proportional

error:- the ratio of the error in $\frac{dC_{A1}}{dt_1}$, to $\frac{dC_{A2}}{dt_2}$. In order to minimize the error, he proposed a procedure for finding an optimum time schedule for making composition measurements. By transforming the time variable to a dimensionless variable, so that the changes in C_A between one sampling time and the next should be equal throughout the course of the experiment, the experimental error was minimized. In principle then, accurate rate data may be obtained from composition-time data.

1.6.4. Analog computer, trial-and-error approach

The rate constants are estimated here by simulation of the mathematical model for the reaction system on an analog computer. The procedures can be outlined as follow:

(1) Construction of a block diagram for connecting the operational elements corresponding to the differential rate equations which described the assumed reaction mechanism.

(2) Selection of the scales for representation of the dependent variable and time.

(3) Calculation of parameters of the model from the coefficients of the original equations and the selected values of the scale.

The criterion generally used, is to select the mathematical model whose characteristics compare most favorably with the experimental curves for the composition of the reaction mixture as a function of time. The curves simulated by the analog computer provide a visual evaluation of the alternative models. An example of this, is given by Katarov and Lutsenko [19]. As the criterion employed in this method, is to compare the shape, the major deficiency of the method lies in discriminating

between various "best fits" for alternative reaction mechanisms.

1.6.5. Approximate solutions for a specific reaction system

Because many addition, substitution and polymerization reactions take the following irreversible consecutive, competitive form:



and because the general solution to the system with any initial composition and any set of constants is still not available, Friedman and White [14] proposed a procedure of transforming the differential rate equations which describe the reaction system, into dimensionless form so that the results would be applicable to a wider variety of systems. They introduced an empirical parameter b which is a function only of $K_i (= \frac{k_i}{k_1})$ to characterize the relationship between β_r and t'_r by the below equation, (1-20)

$$\beta_r = -e^{-bt'_r} \quad (1-20)$$

Then they derived the general approximate solution to the system from the differential rate equations which represent the reaction system in equation (1-21)

$$y_o = \exp\left[\frac{\beta_o}{b} (e^{-bt'_r} - 1)\right] \quad (1-21)$$

$$\beta = \beta_o e^{-bt'_r} \quad (1-22)$$

In equation (1-22), an arbitrary initial value of β is related to the empirical parameter b which is a function only of K_i ($= \frac{k_i}{k_1}$). For K_2 equal or greater than 0.1, the values of parameter b can be calculated from a second-degree multinomial in K_3 and $\log_{10} K_2$. The nature of the dependence of parameter b by the approximate solution is found by fitting the predicted values calculated by equation (1-21) and the experimental data values through the method of least squares.

This approximate solution method handles well the reaction system in equation (1-19) but lacks generalization.

1.6.6. Elimination of time variable from the differential equations

Benson [5], proposed a procedure for eliminating the time variable by dividing each of the differential equations which describe the reaction system by one of these equations. For parallel reaction steps such as,

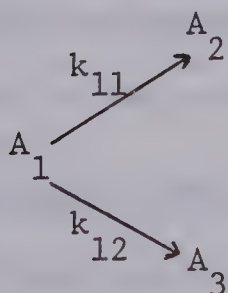


Figure 4. A Parallel Reaction Steps Chemical Model

suppose that the order of reaction for step 1 is n_{11} and for step 2 is n_{12} . Then, the rate equations for the two steps may be represented by,

$$\frac{dC_2}{dt} = k_{11} C_1^{n_{11}} \quad (1-23)$$

$$\frac{dC_3}{dt} = k_{12} C_1^{n_{12}} \quad (1-24)$$

Benson has shown that dividing equation (1-23) by equation (1-24) to eliminate the variable yields

$$\frac{dC_2}{dC_3} = \frac{k_{11}}{k_{12}} C_1^{(n_{11}-n_{12})} \quad (1-25)$$

If $n_{11} = n_{12}$, then direct integration is possible, yielding

$$C_2 = \frac{k_{11}}{k_{12}} C_1 + \phi \quad (1-26)$$

The integration constant, ϕ , is usually zero at zero time. If C_2 and C_3 are produced from identical reactants in which the overall kinetics are of equal order, they will be formed in a constant ratio at all times.

Mezaki [27] points out that because of the experimental error encountered in measuring concentrations, the rate constant calculated by using this method may be erroneous. This is especially true when the reference concentration C_3 of the component cannot be obtained accurately (in equation (1-25)); in this case, the rate constant estimated will deviate very much from the true one. The other obvious disadvantage of using this method is that the rate constants can be obtained only relative to one another.

1.7. Mechanistic modelling using a set of experimental rate data

In the last section, different methods of estimating rate constants for multi-step kinetic models have been discussed. Not much progress has been accomplished in the last decade on the problems of mechanistic modelling, in the strict sense from a set of rate data. In this section some of the most recent works will be examined briefly.

Peterson [29] has outlined a procedure for the classical two-step, consecutive reaction system with an unassigned order of reaction, n_{11} , to the reactant, A_1 and a first order exponent for the second reaction step,

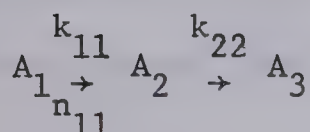


Figure 5 Consecutive reaction system

The differential rate equations are written, using the same nomenclature,

$$\frac{dC_1}{dt} = -k_{11}^{n_{11}} C_1^{n_{11}}$$

$$\frac{dC_2}{dt} = k_{11}^{n_{11}} C_1^{n_{11}} - k_{22} C_2 \quad (1-27)$$

$$\frac{dC_3}{dt} = k_{22} C_2$$

By using non-linear estimation in conjunction with analytic integration, i.e. the method mentioned in section (1.6.1.), the rate constants and order of reaction can be approximated. He has shown how to set up an intermediate mechanism as a stepping-stone towards building a more

adequate mechanistic rate equation for the complex reaction system. The standard deviation of the fit and physical reality of the results (expressed as positive values for the rate constant) are the two criteria used to discriminate between the various plausible models.

Fux and Ioffe [15] in their study of mechanistic modelling claimed that because of the unknown nature of experimental error as well as the unknown values of rate constants for a real reaction system, it is more reasonable to carry out the initial analysis, using a set of simulated data, which characterized the actual kinetic experimental points statistically. At first, true data were generated from a set of differential equations which describe an assumed monomolecular kinetic model in which all the reaction steps follow first-order kinetics,

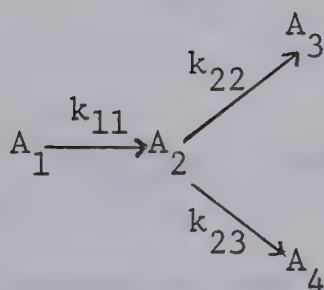


Figure 6 Consecutive and Parallel Reaction System

with initial condition at $t=0$ $C_1=1$, $C_2=C_3=C_4=0$, and with appropriate values for the rate constants. Then normally distributed random error with standard deviations, $s=0.02$; 0.05 ; 0.1 ; 0.15 , respectively, were introduced into the true values. To demonstrate that the true kinetic model can be obtained from the experimental data using their procedure, they have assumed several alternative reaction schemes for their simu-

lated "experimental data". The rate constants of a kinetic model were estimated first by integrating the differential equations which represent the model and then minimizing the sum of the squares of the difference between the integrated values and the simulated "experimental" ones. The adequacy of the assumed reaction scheme in fitting the data was checked by using only positive values of the rate constants as the criterion. If negative rate constants were obtained, the estimation of different values for the negative rate constant was repeated by using simplex method. They have shown a monomolecular reaction scheme of the type,

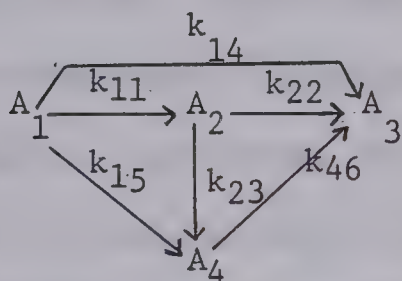


Figure 7 Monomolecular reaction system

can be reduced to the true kinetic model of Figure 6 from the simulated "experimental" data. They also suggested that if an independent experimental study of a particular reaction step were performed, improved and more consistent results can be obtained by calculating the rest of the rate constants in terms of the independently measured value.

CHAPTER II

ANALYSIS OF MULTI-STEP CHEMICAL REACTION SYSTEM

2.1. Introduction

As pointed out in chapter 1 due to the complexity of the chemistry, the various combinations of parallel and consecutive multiple reaction steps possible, and the uncertainty in the reaction order associated with each reacting component, an approach would be desirable here in which a kinetic model may be determined from experimental data so as to reduce the modelling and computational problems encountered in the analysis of multiple-step chemical reaction systems. A semi-empirical approach represents an improvement over strictly empirical methods for developing the model, if one recognizes that kinetic studies of much simpler reaction systems than those cited earlier have not yet departed from a largely empirical correlation point of view.

Numerical differentiation of composition-time kinetic data has attractive features in analyzing complex reaction systems. With the customary "concentration-time" experimental data, Dalla Lana [10] has suggested that the individual steps in multiple-step chemical reaction system be modelled. This would reduce the degree of empiricism associated with procedures requiring direct modelling of the entire system. The modelling procedure can be developed by considering the general form of rate equation shown below,

$$\frac{dC_i}{dt} = \sum_{j=1}^n r_{ij} (C_1, C_2, \dots, C_m) \quad (2-1)$$

in which the contributions to the overall rate of change of one component from each reaction step are summed.

The individual terms in the right-hand-side of equation (2-1), r_{ij} , can each be approximated by a power type of rate equation. This approach is commonly followed in the analysis of simple one-or two-step reaction systems, and gives for each term,

$$r_{ij} = k_{ij} C_i^{n_{ij}} \quad (2-2)$$

for a monomolecular reaction step, $A_i \rightarrow \text{product}$

Local values of the left-hand-side of equation (2-1) are known from numerical differentiation of concentration-time experimental data. When the number of independent ordinary differential equations of the type, equation (2-1), is equal to the number of contributing steps, then local values for each reaction step, r_{ij} , can also be expressed in terms of the known values of $\frac{dC_i}{dt}$. By this approach, the analysis decomposes overall rate data into rate data for individual reaction steps. The use of simple algebraic computations required in this approach to modelling is more attractive computationally than the use of variations in the integral method when the set of differential equations has to be solved simultaneously to check the assumed model.

The remainder of this section will provide the groundwork for the subsequent applications of the proposed techniques. Before trying to demonstrate the applicability of this approach, a brief survey of numerical differentiation methods, and a method of obtaining accurate first derivatives in the situation when a small amount of data are available will be presented. Following this, time-composition data

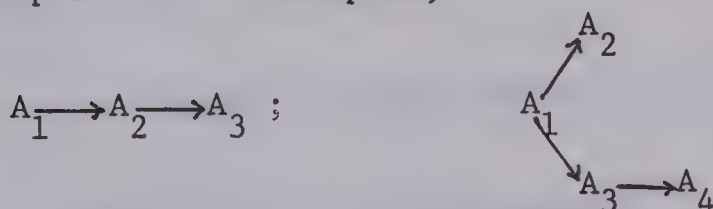
generated from a numerical solution to a hypothetical non-linear kinetic model, plus normally distributed random error will be used as a first demonstration to examine the applicability and the accuracy of the proposed approach. To complete this study, the method is applied to several real reaction systems, the data for which are reported in the literature.

2.2. Classification and analysis of complex reaction systems

The system of algebraic equations, which must be solved for various kinetic models can be classified into one of three cases, depending upon the "chemical model" involved:

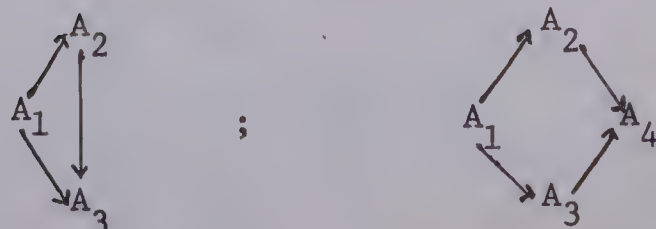
2.2.1. Open network reaction systems (intermediate or final product components do not form from two or more converging reaction step):

Open network examples,

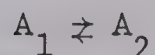


2.2.2. Closed (or loop) reaction system (intermediate or final product components may form from two or more converging reaction steps):

Examples of closed (or loop) reaction systems,



2.2.2.1. Reversible reaction system (subclassification
of 2.2.2.)



2.2.3. Combinations of 2.2.2.1., with 2.2.1. or 2.2.2. or both

In the analysis immediately following this, the reaction rate component, $\frac{dC_i}{dt}(=r_i)$, is assumed to be known from the differentiation of the experimental composition-time data.

2.2.1. Open network reaction systems

Suppose a reaction system follows the chemical model shown below:

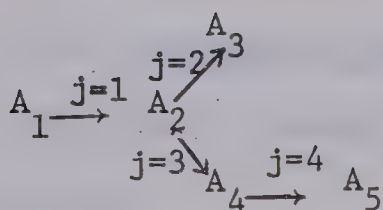


Figure 8 An Open Network Chemical Model

The reaction rate components, $\frac{dC_i}{dt}$, ($i=1, \dots, 5$), all measured at a specific reaction time are each equivalent to the algebraic sum of the rates for each contributing reaction step, r_{ij} . Mathematically, the set of $\frac{dC_i}{dt}$ can be expressed in the following form, where r_i is now used as an abbreviated notation for $\frac{dC_i}{dt}$:

$$r_1 = -r_{11}$$

$$r_2 = r_{11} - r_{22} - r_{23}$$

$$r_3 = r_{22}$$

(2-3)

$$r_4 = r_{23} - r_{44}$$

$$r_5 = r_{44}$$

Since all r_i are available from the differentiated experimental data and since only four unknown reaction steps occur on the model shown in Figure 8, for a common "time", local values of rates for each reaction step, r_{ij} , can be obtained simply by solving the set of equations (2-3). This procedure is used to generate a set of r_{ij} at a number of different times, in effect, providing a set of rate data for each independent reaction step. The chemical model of Figure 8 may be completely defined upon estimating all k_{ij} and n_{ij} by regression techniques.

2.2.2. Closed (or loop) reaction systems

The rates of overall reaction for a reaction system with the chemical model,

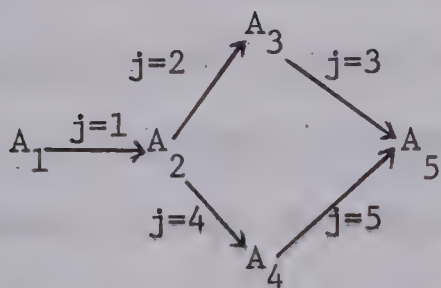


Figure 9 Chemical Model for a Closed Reaction System

can be described mathematically, at a common time, as shown below:

$$r_1 = -r_{11}$$

$$r_2 = r_{11} - r_{22} - r_{44}$$

$$r_3 = r_{22} - r_{33}$$

(2-4)

$$r_4 = r_{24} - r_{45}$$

$$r_5 = r_{33} + r_{45}$$

In matrix form, equations (2-4) may be written,

$$\begin{pmatrix} r_1 \\ r_2 \\ r_3 \\ r_4 \\ r_5 \end{pmatrix} = \begin{pmatrix} r_{11} \\ r_{22} \\ r_{33} \\ r_{24} \\ r_{45} \end{pmatrix} \begin{pmatrix} -1 & 0 & 0 & 0 & 0 \\ 1 & -1 & 0 & -1 & 0 \\ 0 & 1 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 & -1 \\ 0 & 0 & 1 & 0 & 1 \end{pmatrix} \quad (2-5)$$

$$\bar{r}_i = \bar{r}_{ij} \cdot \bar{M} \quad (2-6)$$

Since the determinant of the coefficient matrix, \bar{M} , is zero the matrix is singular and the inverse matrix, $(\bar{M})^{-1}$, does not exist. The \bar{r}_{ij} column cannot be solved explicitly. Farkas [9] has solved a similar loop reaction system in which all the reaction steps follow first-order kinetics, as described in chapter 5, by assuming values for the relative rate constants for the branching reaction rate steps. Of course, the values of rate constants obtained in this way will not be absolute values and further, similar values for the reaction order of both branching steps are required. Experimentally, this problem can be overcome by performing an independent kinetic study for one of the intermediate components under similar reaction conditions.

In this work, for kinetic models of loop reaction system it is proposed to estimate the parameters (the rate constant and order of

reaction) of two reaction steps by non-linear estimation. This can be visualized by considering the component, A_2 , in Figure 9. The first two equation of (2-4) yield,

$$r_2 + r_1 = -r_{22} - r_{24} \quad (2-7)$$

Then, using power function approximation to the two r_{ij} one obtains,

$$r_2 + r_1 = -k_{22} C_2^{n_{22}} - k_{24} C_2^{n_{24}} \quad (2-8)$$

Since $(r_2 + r_1)$ and C_2 are known values, the parameters, k_{22} , n_{22} , k_{24} , and n_{24} , can be obtained by non-linear estimation. Once the r_{22} and r_{24} parameters are known, the remainder of the reaction steps, r_{ij} , in equation (2-4) can be evaluated by algebraic substitution. The components with higher concentration values are usually chosen for the non-linear estimation. The reason for this preference will be demonstrated in section (4.4.1.).

2.2.2.1. Reversible reaction system

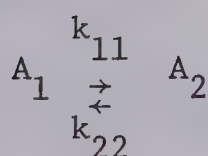


Figure 10 Reversible reaction system

Rate balances around each reacting component are given by:

$$\begin{aligned} r_1 &= -r_{11} + r_{22} \\ r_2 &= r_{11} - r_{22} \end{aligned} \quad (2-9)$$

In matrix form, the equations become

$$\begin{pmatrix} r_1 \\ r_2 \end{pmatrix} = \begin{pmatrix} r_{11} \\ r_{22} \end{pmatrix} \begin{pmatrix} -1 & 1 \\ 1 & -1 \end{pmatrix} \quad (2-10)$$

$$\bar{r}_i = \bar{r}_{ij} \cdot \bar{M} \quad (2-11)$$

It is obvious that the determinant of the coefficient matrix of equation (2-10) is zero, therefore r_{11} and r_{22} cannot be evaluated explicitly. Both rates can be determined only when there is an independent means of specifying the value of one parameter or the ratio of parameters. The thermodynamic equilibrium constant, preferably experimentally determined, might provide such information. In the absence of knowledge about the equilibrium constant, the rate step can be determined by applying the same procedure as described in section 2.2.2., i.e. estimating k_{11} , n_{11} , k_{22} , and n_{22} from either one of the equations in (2-9) by non-linear estimation.

The validity of this procedure for sections (2.2.2.) and (2.2.2.1.) will be examined by applying this approach to some actual experimental reaction data. These will be presented in the final chapter.

2.2.3. Combination of reversible and loop reaction system

For a reaction system of the type,

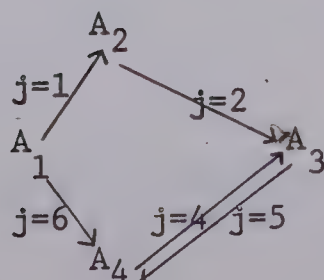


Figure 11 Reversible and Loop Reaction System

the chemical model may be determined by first applying the non-linear estimation procedure to the reversible step as outlined in section (2.2.2.1.), and subsequently analyzing the remaining reaction steps of the system as described in section (2.2.2.).

The method of analysis of the data described in section (2.2.) has little value if the accuracy of numerical differentiation of experimental data cannot be assured. A brief survey of the available methods for numerical differentiation, the importance of smoothing the experimental data before differentiation, and a method of obtaining correct first derivatives from a limited set of experimental data will be presented in the following chapter.

CHAPTER III

DATA SMOOTHING AND NUMERICAL DIFFERENTIATION

3.1. Introduction

The measurement of experimental data is always subject to errors. These errors, may be sufficiently large sometimes that the algebraic sign of the first derivatives, obtained by differentiating the data using a simple difference technique, is incorrect. This situation can be visualized by considering the example of Figure 12 taken from Ralston [31]

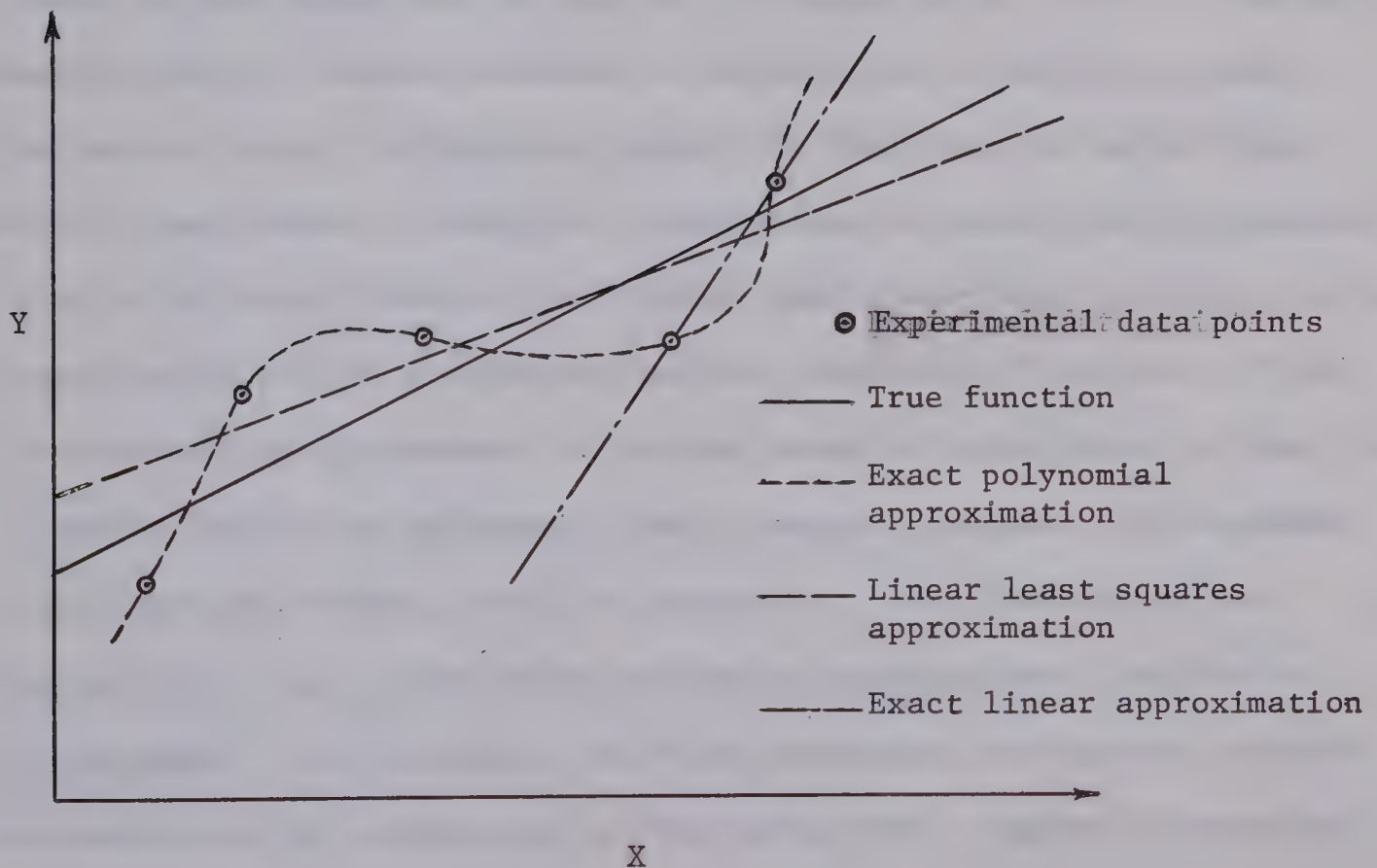


Figure 12 Least squares and exact approximation

The five empirical points employed by Ralston possess, in fact, a linear relationship between X and Y. Since the errors in the data are quite significant, linear approximations using any two points will lead to very poor approximations to the true function. The sign of the first derivatives, obtained by linear approximation, will be different from that of the true function. Although the fourth order polynomials approximation (exact fit) does not deviate very much, the first derivatives are very different from the comparable derivatives for the true function. In the case shown, the linear least squares approximation lies close to the true function with a similar slope.

Thus, it is essential to smooth the experimental data before it is differentiated. Walas [36] and [3] also stressed the important role played by data smoothing in numerical differentiation. With the advancement of digital computer methods, it is no longer justified to smooth the data by hand. Furthermore, though the least squares method works well in many cases, it does not always produce a satisfactory representation of the data. Ralston [32] claimed that a non-linear function can be approximated well by a straight line over subranges of the data. This is true only in the presence of a large number of data points so that the linearity within the subranges is well assured. Lanczos [22] suggested a procedure of "movable strip" or moving arc, i.e. evaluating the derivative at each center point and moving stepwise down from the top of the data. In this method, the first derivative can only be obtained accurately at the center point of the moving arc. Suppose a five-point moving arc is used: then there will be a loss of four data points (the first two points and the last two points) for the first derivatives at

these points cannot be evaluated accurately with this approach. The method, as a result, may not be suitable for correlating kinetic data (time-composition) of complex reaction systems because the data are generally obtained in a limited amount. Thus, the problem becomes how to select a function, generally nonlinear, that will approximate the limited amount of complex reaction kinetic data (say seven or eight points).

Many types of functions are available for fitting purposes. In the following section, a brief review of some methods employing the most commonly used polynomial functions, will be presented.

3.2. Polynomial Approximations

For polynomial approximations, the following three general types can be classified:

3.2.1. Interpolation approximations

3.2.1.1. Newton's interpolation formulae with equal spacing [8]

3.2.1.2. Lagrangian functions [8]

3.2.2. Least squares polynomial approximations [23]

3.2.3. Minimization of the maximum error polynomial approximations [32]

3.2.1.1. Newton's Interpolation Formulae

For a set of equally spaced h , $x_0, x_1, \dots, x_n, x_{n+1}$ points, using Newton's forward difference formula, the function $f(x)$ can be approximated by $p(x)$ as follow [8]:

$$f(x) \approx p(x) = f_0 + \binom{s}{1} \Delta f_0 + \binom{s}{2} \Delta^2 f_0 + \dots + \binom{s}{n} \Delta^n f_0 \quad (3-1)$$

$$\text{where } s = \frac{x-x_0}{h},$$

$$\Delta f_0 = f_1 - f_0, \quad f_0 = p_1(x_0), \quad f_1 = p_1(x_1)$$

The crucial weakness of this method lies in the inverse proportionality of round-off error and truncation error to the equal spaced interval h , i.e. by decreasing the value of h so as to reduce the truncation error, the error caused by round-off will magnify. Although an optimum choice of h may sometimes be made when the two error-bounds are equally good, the dominant error source lies on the input errors themselves. From the numerical differentiation point-of-view, as pointed out in section (3.1.), exact polynomial approximation may not be suitable.

3.2.1.2. Lagrangian Functions

This method is useful when the data are not equally spaced. Using Lagrange's interpolation formula, the function $f(x)$ can be approximated by,

$$f(x) \approx p(x) = \sum_{i=0}^n L_i(x) y_i \quad (3-2)$$

$$\text{where, } L_i(x) = \frac{\prod_{\substack{j=0 \\ j \neq i}}^n (x-x_j)}{\prod_{\substack{j=0 \\ j \neq i}}^n (x_i-x_j)} \quad (3-3)$$

are called Lagrangian interpolation polynomials

$$y_i = p(x_i), \text{ for each } x_i, i=0,1, \dots, n$$

The disadvantages of using this approximation are:

(1) the coefficients of the polynomial $L_i(x)$ are dependent on each other, i.e. the addition of one more term to the polynomial will require a complete recalculation.

(2) values of $L_i(x)$ are obtained by taking the difference between data points very close to one another.

3.2.2. Least squares Polynomial approximations [23]

Suppose a function, $f(x_i)$, with discrete data points, $i=1,2, \dots, n$, can be represented by equation (3-4)

$$f(x_i) = \sum_{j=0}^m \alpha_j p_j(x_i) + e_i \quad (3-4)$$

The principle of this approximation is to minimize

$$\sum_{i=1}^n e_i^2$$

so as to yield best estimate values for α_j

3.2.2.1. Simple Power Functions

In this case a power series is substituted for $p_j(x_i)$ so that equation (3-4) becomes

$$f(x_i) = \sum_{j=0}^m \beta_j x_i^j + e_i \quad (3-5)$$

where β_j are the coefficients of the power series

Lapidus [23] has shown that by minimization of the sum of the squares of the error terms, i.e. if $S_m^2 = \sum_{i=1}^n e_i^2 \geq 0$ (3-6)

$$\text{and, } \frac{d(s_m^2)}{d\beta_j} = 0 \quad (3-7)$$

The following set of simultaneous equations written in matrix form results,

$$\bar{X}^T \bar{X} \bar{B} = \bar{X}^T \bar{Y} \quad (3-8)$$

$$\text{where } \bar{X}^T \bar{X} = \begin{pmatrix} n & \sum x_i & \sum x_i^2 & \dots & \sum x_i^m \\ \sum x_i & \sum x_i^2 & \sum x_i^3 & \dots & \sum x_i^{m+1} \\ \sum x_i^2 & \sum x_i^3 & \dots & \dots & \sum x_i^{m+2} \\ \dots & \dots & \dots & \dots & \dots \\ \sum x_i^m & \sum x_i^{m+1} & \dots & \dots & \sum x_i^{m+m} \end{pmatrix} \quad (3-9)$$

$$\text{and } \bar{X}^T \bar{Y} = \begin{pmatrix} \sum f_i \\ \sum x_i f_i \\ \sum x_i^2 f_i \\ \dots \\ \sum x_i^m f_i \end{pmatrix} \quad (3-10)$$

\bar{B} is the vector of the unknown coefficients, β_j .

The power coefficients, \bar{B} , are usually determined by Gauss elimination.

3.2.2.2. Orthogonal Polynomials

Orthogonal polynomials sometimes are a useful tool for approximating a function because of the following features:

- (1) the solution of the linear equation is guaranteed
- (2) the coefficients of the polynomials are independent of each other, i.e. increasing the power of polynomials does not change the previously calculated coefficients [40].

Using an orthogonal polynomial $Q_j(x_i)$ to approximate $f(x_i)$ for discrete data points $(i=1,2, \dots, n)$, the use of a least squares criterion gives

$$f(x_i) = \sum_{j=0}^m \gamma_j Q_j(x_i) + e_i \quad (3-11)$$

In the same manner as before, the least-squares minimization leads to

$$\min \sum_{i=1}^n e_i^2 \geq 0 \quad (3-12)$$

When numerically differentiating relatively smooth equal-spaced data, gram orthogonal polynomials proved to be quite effective and convenient [40]. The coefficients of the gram orthogonal polynomials for evenly spaced data points are previously calculated and the need to solve a set of linear equations is eliminated. When the data points are smooth and exact, a second-degree polynomial or parabolic approximation is found to be adequate. A method of testing the quality of the fit and a formula for calculating the standard error of derivatives attributed to the experimental error have been developed [40]. In practice, irregular data points give fluctuating and inconsistent results.

3.2.3. Minimization of the Maximum Error Approximation [32]

As the title of this section expresses, the basic idea involved in this method is to minimize the maximum error that arises due to the use of an approximation. The error term, e_i , for discrete data, x_i, y_i ,

where $i=1,2,3, \dots, n$, can be expressed as shown below,

$$e_i = f(x_i) - y_i \quad (3-13)$$

If we assume $f(x_i)$ is the function that approximates the data points and if E is the largest error among e_i , then the object of this method is to determine $f(x_i)$ for which E is smallest. The minimum maximum approximation is also called a Chebyshev approximation.

As for what type of function to be chosen for minimum maximum error approximation, Ralston [32] presents a full account of the more accurate results obtained with a rational function which is made up of the ratio of two polynomials rather than the original polynomials. He has also developed a technique for generating a rational approximation which, among all rational approximations with the same degree polynomials in the numerator and in the denominator, gives the minimum maximum error.

The method of smoothing cited in section (3.2.1.) are unsuitable for numerical differentiation. Although least squares method (section (3.2.2.)) smooth the data reasonably well, the first derivatives evaluated from the resulting least squares approximation sometimes give erroneous values (this can be seen in section (4.3.)).

In view of the following problem: the non-linearity of time-composition relationship and the availability of only-limited amount of data, it will be advisable to fit a linear or non-linear function which essentially has a shape similar to the set of time-composition data. Subsequently, the derivatives are obtained by analytical or numerical differentiation of the resulting function.

In relation to this, Mezaki and Kittrell [28] have shown the advantages of fitting a non-linear function to a set of conversion-space

time data which have non-linear relationship. They fit

$$x = A \tanh[B(\frac{W}{F})] \quad (3-14)$$

to the data, and analytically differentiate the function at the origin. The parameters, A and B, define the function which was fitted by non-linear least squares. They found that by including the high conversion as well as the low conversion non-linear data, they could discriminate between two rival models. On the other hand, the discrimination cannot be done if the linearity of the data was assumed.

In this work, the parameters of the non-linear function fitted to the data are approximated by minimizing the residual sum of squares using Rosenbrock's Hill-Climbing Method. [34].

A brief review of the Hill-Climbing method and some of its modification will be described in the following paragraph.

3.3. Optimizing by Hill-Climbing Method [34]

The optimization of a function arises in many ways in engineering application. Some of the common methods can be summarized as follow:

3.3.1. Steepest Ascent or Descent Method

In this method [34], the partial derivatives of a function $f(x_1, x_2, \dots, x_p)$ are first found by using a set of p experiments, i.e. if x_1 is first varied by an amount of α_1 , then $\frac{\partial f}{\partial x_1}$ can be approximated by,

$$\left. \frac{\partial f}{\partial x_1} \right|_{\bar{x}=\bar{a}} \approx \frac{f(a_1 + \alpha_1, a_2, \dots, a_p) - f(a_1, a_2, \dots, a_p)}{\alpha_1} \quad (3-15)$$

Subsequently, the remaining derivatives are estimated in the same way. Then the direction of steepest ascent is found by calculating the

unit vector \bar{L} with components

$$l_i = \frac{\partial f / \partial x_i}{\left[\sum_{j=1}^p (\partial f / \partial x_j)^2 \right]^{1/2}} \quad (3-16)$$

When $p=2$, the procedure can be illustrated in Figure 13.

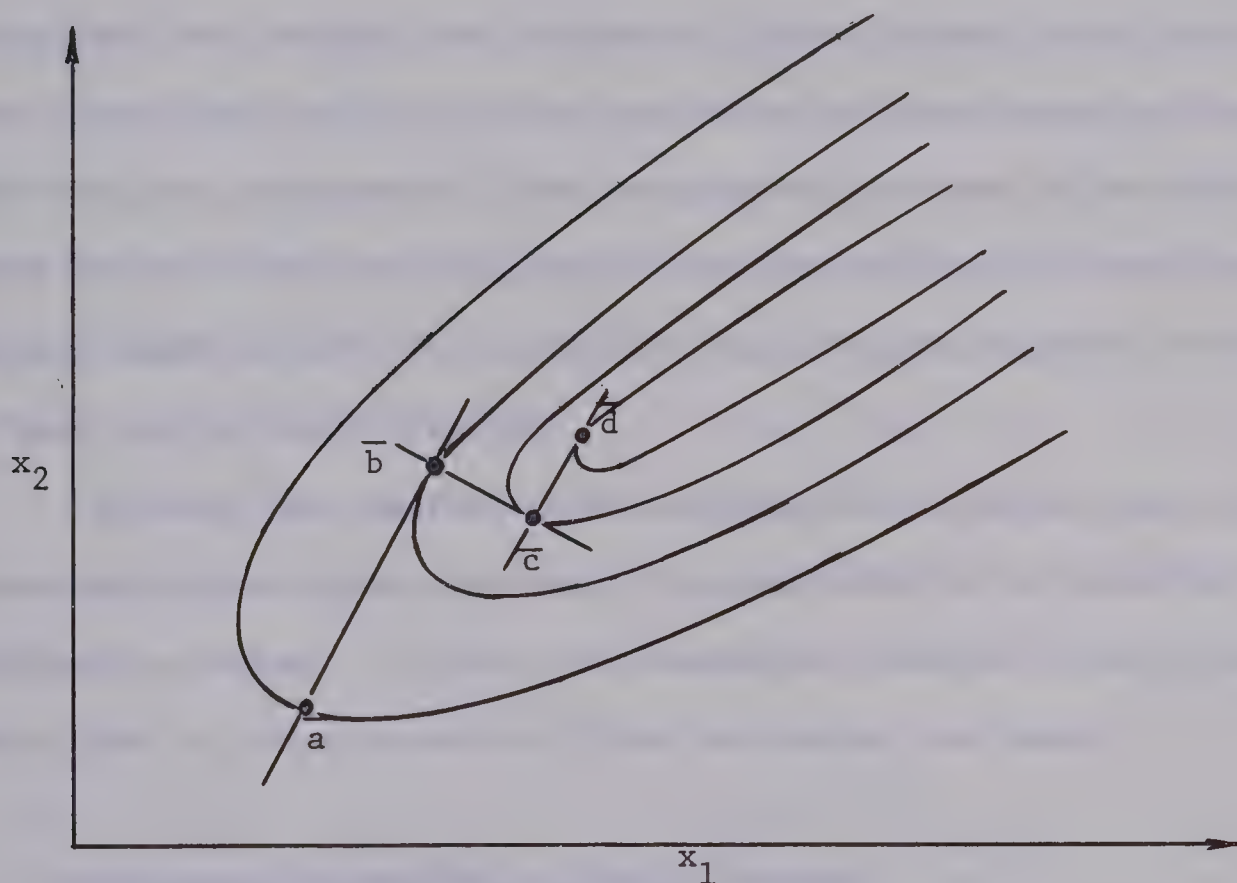


Figure 13 Procedure of Steepest Ascent Method

then the highest point \bar{b} , on the line estimated from the initial point \bar{a} , in the direction of \bar{L} , is found. The whole process is repeated again by treating \bar{b} as an initial point. The search is carried out until the summit, \bar{d} , is reached.

3.3.2. Rosenbrock's Method of Hill-Climbing

Rosenbrock [34] modified an accelerated Hill-Climbing method by introducing a variable scaling factor. After each new function evaluat-

ion, the values of the function, f , so obtained is compared with the best previous value. If the operation was successful in increasing the function value, the value of the step length, e , is trebled in the favorable coordinate direction. If it was unsuccessful, e is multiplied by $-\frac{1}{2}$. The effect of this modification is that if a change parallel to \bar{u}_i orthogonal unit vector, (i being a component of a set of p orthogonal unit vectors) was successful, then the next trial is made in this direction it will be in the same sense and three times as long. If the trial was unsuccessful, then the step will be made in the opposite sense and will have half the length. So the operation of searching the optimum point in fact tries to explore on each line, instead of taking a fixed step in each direction.

Although the progress of Rosenbrock's method may be slow when there are narrow ridges, because of its generality it is relatively difficult to defeat. In this work Rosenbrock's method of Hill-Climbing, which does not require analytic first derivative, was used.

3.4. Minimizing the Residual of Sum of Squares

The choice of an approximating function has to be made on the basis of experience and intuition [33]. The conventional resolving power of polynomials or trigonometric sums are not practical for numerical differentiation. Even though they might represent the experimental data faithfully.

Some common functions, $Y=f(x)$, that generally have similar shapes to the time-composition kinetic data, were drawn by an IBM 1627 plotter using the appropriate values of parameters of the functions. These

curves are as shown in Appendices (1) and (2). Their use helps to choose an appropriate function that will best serve the particular case. Sometimes, the accuracy of approximation can be improved simply by adding another identical term to the previous function, as illustrated in the case of 2 and 3 in Appendix (1). Generally, if the fitted function behaves reasonably well compared to the experimental data, three to four parameters are accurate enough to determine the approximate function. The use of too many parameters approaches the case of high power polynomials and at the same time, computing time increases immensely. Computing time here in general is a function of the total number of data points, the number of the parameters in the fitted function and the values of the initial guess introduced. The computing time for a function of 4 parameters to approximate a set of data (say 15 points) with initial guess of unity in an IBM 360/67 will vary from 2 to 4 minutes.

At the end of the searching operation for a fitted function, the variance of the fit and the deviation between the observed experimental data and the calculated values from the function are recorded. The variance is defined as:

$$s^2 = \frac{\sum_{i=1}^N (C_{i,\text{obser.}} - C_{i,\text{calcn.}})^2}{N-P} \quad (3-17)$$

The variance was primarily used as a measure of the quality of fit of the function to the experimental data. It may be difficult to choose an optimum function from two functions having almost equal variance. In this case, the checking of material balance, i.e. the

composition data regenerated from the fitted function, may help one to select a function which is consistent with the reaction system. A practical case encountered in this work will be presented in the later section. As a rule, the material balance is always checked after optimum functions for all reacting components have been obtained.

The superiority of using the smoothing technique of minimizing the residual sum of squares using Rosenbrock's Hill-Climbing method over the conventional least squares polynomial approximations will be presented in chapter 4.

3.5. Data Smoothing by Minimizing the Residual Sum of Squares and Differentiating the Smooth Function

The procedure for differentiating of experimental data to be used in this work is now summarized as shown below:

- STEP 1. A linear or non-linear function, which essentially has similar shape to that of the time-composition data is fitted to the data.
- STEP 2. The parameter(s) of the fitted function are determined by minimizing the residual sum of squares using Rosenbrock's Hill-Climbing method (section 3.3.2.)
- STEP 3. The resulting smooth function thus obtained is analytically or numerically differentiated.

CHAPTER IV

A NON-LINEAR HYPOTHETICAL KINETIC MODEL

4.1. Generating Kinetic Data

To examine the accuracy of the numerical differentiation technique by minimizing the residual sum of squares using Rosenbrock's Hill-Climbing method (section 3.5.), and the kinetic analysis approach as developed in section (2.2.) for complex reaction systems, a non-linear hypothetical chemical reaction system, whose rate parameters are known a priori, will be used as a reference system:

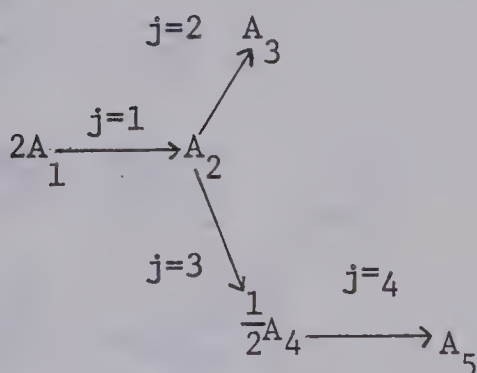


Figure 14

Based on this model, time-composition data may be generated by assigning fixed values to the set of reaction rate constants. It is assumed that the stoichiometric coefficient of each reacting component is equal to the order of the reaction for that component. The object of assuming a non-linear model is to demonstrate the validity of this kinetic approach (section 2.2.) i.e. that the order of reaction of each reacting component can be obtained directly from the analysis of the data without preassigning any value to the order. Generally, information on the value of the reaction order is not available to the kineticist

(especially for heterogeneous catalytic reaction systems). The model shown in Figure 14 will also be used to illustrate that the approach of section (2.2.) treats the time-composition data equally accurate, irrespective of the concentration levels, if sufficient data points are available. Mathematically, the reaction rate of each reacting component for the reaction system of Figure 14 can be expressed by the equation,

$$\begin{aligned}\frac{dC_1}{dt} &= -k_{11}C_1^2 \\ \frac{dC_2}{dt} &= \frac{k_{11}}{2}C_1^2 - (k_{22} + k_{23})C_2 \\ \frac{dC_3}{dt} &= k_{22}C_2 \\ \frac{dC_4}{dt} &= \frac{k_{23}}{2}C_2 - k_{44}C_4^{0.5} \\ \frac{dC_5}{dt} &= 2k_{44}C_4^{0.5}\end{aligned}\tag{4-1}$$

The pre-assigned values for the rate constants and the initial conditions are given below (in self-consistent units):

$$\begin{aligned}k_{11} &= 1.4, & k_{22} &= 0.09 \\ k_{23} &= 0.25, & k_{44} &= 0.04\end{aligned}\tag{4-2}$$

$$\text{At time } t=0, C_1=1.0 \text{ mole/litre, } C_2=C_3=C_4=C_5=0\tag{4-3}$$

The simultaneous non-linear differential equations (4-1) were numerically integrated by Fourth-order Runge-Kutta (or Rung-Kutta-

Simpson method). With the interval, $h=0.002$, the accuracy of the integration is well assured, as can be seen from the negligible difference between values obtained by analytical and numerical integration for the concentration, C_1 . The material balance column in Table 1 also provides a check since at any specific reaction time the equivalent number of moles of component, A_1 , must remain constant.

The time-composition data thus obtained were simulated according to the procedure described in the following section.

4.2. Simulation of Experimental Data

First of all, uniformly distributed random number, x_i , are generated by using IBM 1130 scientific subroutine RANDU and then they are inserted into the following equation (4-4) to calculate random number, E which are normally distributed around the true values, μ .

$$E = \frac{\sum_{i=1}^N x_i - \frac{N}{2}}{\sqrt{N/2}} \quad (4-4)$$

Here, E approaches the normal distribution about the true (or mean) value, μ , asymptotically as N approaches infinity. With the given true, mean value (μ), standard deviation (s) is defined by equation (4-5).

$$s = e\mu \quad (4-5)$$

$$\text{Then } Y = Es + \mu \quad (4-6)$$

The standard deviation $s = e\mu$ defined in this fashion, corresponds somewhat to the constant per cent error experienced in most procedures of chemical analysis and the term Es in equation (4-6) is equivalent to the normally distributed random error introduced. For $e=0.03$, as the confidence coefficient, $Z_c=2$, at a 95% confidence level, $Y=\mu \pm 2s$, or,

TABLE 1
INPUT DATA

K11=1.40 K22=0.09 K23=0.25 K44=0.04
K111=K11/2 KK23=K23/2

INITIAL CONDITION

TIME=0.0 (HR.) INTERVAL H = 0.002

A10 = 1 (MOLE/LITRE) A2 = A3 = A4 = A5 = 0.0 (MOLE/LITRE)

REACTION TIME (HR.)	A1	A2	A3	A4	A5	MATERIAL* BALANCE	TRUE A1** MOLE/LITRE
1.01	0.416660	0.235476	0.014869	0.017651	0.006001	0.999956	0.416670
1.51	0.322572	0.241604	0.025697	0.029621	0.012138	0.999932	0.322588
2.01	0.263147	0.230991	0.036368	0.040691	0.019641	0.999910	0.263166
2.51	0.222209	0.213604	0.046386	0.050334	0.028182	0.999887	0.222231
3.01	0.192292	0.193901	0.055558	0.053405	0.037518	0.999863	0.192316
3.51	0.169474	0.174033	0.063833	0.064926	0.047459	0.999827	0.169499
4.01	0.151495	0.155057	0.071225	0.069997	0.057856	0.999762	0.151523
4.51	0.136964	0.137470	0.077794	0.073757	0.068583	0.999688	0.136993
5.01	0.124975	0.121468	0.083606	0.076351	0.079541	0.999609	0.125007
5.51	0.114916	0.107084	0.088735	0.077920	0.090648	0.999529	0.114949
6.01	0.106354	0.094262	0.093252	0.073599	0.101836	0.999450	0.106389
6.51	0.098979	0.082901	0.097226	0.078513	0.113042	0.999368	0.099016
7.01	0.092560	0.072877	0.100719	0.077775	0.124219	0.999291	0.092598
7.51	0.086921	0.064063	0.103788	0.076486	0.135324	0.999215	0.086962
8.01	0.081930	0.056335	0.106486	0.074736	0.146318	0.999150	0.081972
8.51	0.077480	0.049567	0.108858	0.072605	0.157169	0.999086	0.077524
9.01	0.073487	0.043648	0.110944	0.070162	0.167851	0.999023	0.073534
9.51	0.069886	0.038474	0.112782	0.067472	0.178338	0.998960	0.069934
10.01	0.066620	0.033955	0.114402	0.064585	0.188610	0.998896	0.066671

*TOTAL NUMBER OF MOLE/LITRE EQUIVALENT TO A10 PRESENT IN THE REACTION SYSTEM

AT A COMMON INSTANTANEOUS TIME = A1 + 2*A2 + 2*A3 + 4*A4 + 2*A5

**ANALYTICAL EXACT INTEGRATION

$\mu \pm 0.06\mu$, i.e. a 6% error in the analysis. Similarly, for $e=0.05$, a 10% error in the analysis will be simulated. In this manner, the data can be simulated with accuracy as well as the exact knowledge of the true values of each rate constant and reaction order. The simulated concentration data thus obtained were tabulated in Table 2 against their corresponding true values.

4.3. Comparison of Accuracy of Least Squares Polynomial Smoothing Technique with the Method in section 3.5.

Before the method of minimizing the residual sum of squares using Rosenbrock's Hill-Climbing method as described in section (3.5.) is applied to the analysis of the simulated data for the assumed hypothetical model, the accuracy of the method was checked. A comparison with conventional linear-least-squares second, third, and fourth order polynomial approximations was also provided. For this purpose, component A_3 , in Figure 14, was simulated by adding 10% normally distributed random error to the true values. These data are also shown in Table 2.

In the present method, the function,

$$k_1 e^{k_2 T} + k_3 \tanh(k_4 T)$$

was fitted to the data, and the computer output is as shown in Table 3. The computed values of linear-least-squares second, third, and fourth order polynomial approximations are provided in Table 4, 5, and 6.

The smooth data regenerated from the resulted function were listed under the title of "present method" in Table 7. The differences between this smooth data and the true values are almost negligible. The smooth data regenerated from the linear-least-squares second, third, and fourth order polynomials were also recorded in the extreme right three columns. The plots of the smooth curves obtained by these two methods against the

TABLE 2
CONCENTRATION DATA USED IN THIS WORK

REACTION TIME (HR.)	A1	A2	A3	A4	A5	REMARKS
1.000	0.41666 0.41602	0.23547 0.22638	0.01486 0.01522 0.01547	0.01765 0.01808	0.00600 0.00614	TRUE 6 PER CENT ERROR* 10 PER CENT ERROR*
1.500	0.32257 0.33850	0.24160 0.25353	0.02569 0.02480 0.02421	0.02962 0.02859	0.01213 0.01171	TRUE 6 PER CENT ERROR* 10 PER CENT ERROR*
2.000	0.26314 0.26297	0.23099 0.23084	0.03636 0.03704 0.03749	0.04069 0.04145	0.01964 0.02000	TRUE 6 PER CENT ERROR* 10 PER CENT ERROR*
2.500	0.22220 0.22676	0.21360 0.21798	0.04638 0.04619 0.04607	0.05033 0.05012	0.02818 0.02806	TRUE 6 PER CENT ERROR* 10 PER CENT ERROR*
3.000	0.19229 0.19164	0.19390 0.19325	0.05555 0.05464 0.05403	0.05840 0.05744	0.03751 0.03689	TRUE 6 PER CENT ERROR* 10 PER CENT ERROR*
3.500	0.16947 0.16904	0.17403 0.17358	0.06383 0.06396 0.06404	0.06492 0.06505	0.04745 0.04754	TRUE 6 PER CENT ERROR* 10 PER CENT ERROR*
4.000	0.15149 0.14793	0.15505 0.15140	0.07122 0.07562 0.07855	0.06999 0.07431	0.05785 0.06142	TRUE 6 PER CENT ERROR* 10 PER CENT ERROR*
4.500	0.13696 0.13106	0.13747 0.13155	0.07779 0.07727 0.07692	0.07375 0.07325	0.06858 0.06812	TRUE 6 PER CENT ERROR* 10 PER CENT ERROR*
5.000	0.12497 0.12024	0.12146 0.11686	0.08360 0.08176 0.08054	0.07635 0.07467	0.07954 0.07779	TRUE 6 PER CENT ERROR* 10 PER CENT ERROR*
5.500	0.11491 0.11132	0.10708 0.10373	0.08873 0.09025 0.09127	0.07792 0.07926	0.09064 0.09220	TRUE 6 PER CENT ERROR* 10 PER CENT ERROR*

TABLE 2..... Cont'd
CONCENTRATION DATA USED IN THIS WORK

REACTION TIME (HR.)	A1	A2	A3	A4	A5	REMARKS
6.000	0.10635 0.11130	0.09426 0.09865	0.09325 0.08688 0.08263	0.07859 0.07322	0.10183 0.09487	TRUE 6 PER CENT ERROR* 10 PER CENT ERROR*
6.500	0.09897 0.10222	0.08290 0.08562	0.09722 0.09608 0.09533	0.07851 0.07759	0.11304 0.11172	TRUE 6 PER CENT ERROR* 10 PER CENT ERROR*
7.000	0.09256 0.09446	0.07287 0.07437	0.10071 0.10152 0.10207	0.07777 0.07840	0.12421 0.12521	TRUE 6 PER CENT ERROR* 10 PER CENT ERROR*
7.500	0.08692 0.08575	0.06406 0.06320	0.10378 0.10689 0.10897	0.07648 0.07877	0.13532 0.13938	TRUE 6 PER CENT ERROR* 10 PER CENT ERROR*
8.000	0.08193 0.08387	0.05633 0.05766	0.10648 0.10531 0.10453	0.07473 0.07390	0.14631 0.14470	TRUE 6 PER CENT ERROR* 10 PER CENT ERROR*
8.500	0.07748 0.07870	0.04956 0.05034	0.10885 0.10678 0.10540	0.07260 0.07122	0.15716 0.15417	TRUE 6 PER CENT ERROR* 10 PER CENT ERROR*
9.000	0.07348 0.07416	0.04364 0.04404	0.11094 0.10859 0.10702	0.07016 0.06867	0.16785 0.16429	TRUE 6 PER CENT ERROR* 10 PER CENT ERROR*
9.500	0.06988 0.06856	0.03847 0.03774	0.11278 0.11092 0.10969	0.06747 0.06636	0.17833 0.17540	TRUE 6 PER CENT ERROR* 10 PER CENT ERROR*
10.000	0.06662 0.06512	0.03395 0.03318	0.11440 0.11725 0.11916	0.06458 0.06619	0.18861 0.19331	TRUE 6 PER CENT ERROR* 10 PER CENT ERROR*

*WITHIN 95 PER CENT CONFIDENT LEVEL

Table 3

A3 COMPONENT
-- -----

FUNCTION = K1*EXP(K2*T)+K3*TANH(K4*T)

ROTATION NO.	PARAMETER ESTIMATES BY ROSENBROCK METHOD				COUNT
	K1	K2	K3	K4	
1	-0.16100F-01	-0.11085E	01 0.12284E	00 0.16292E	00 0.19068F-04 0.14700E 03
2	-0.16957F-01	-0.11559E	01 0.12281E	00 0.16301E	00 0.19059F-04 0.23100E 03
3	-0.17093F-01	-0.11448E	01 0.12267E	00 0.16353E	00 0.19030F-04 0.31100E 03
4	-0.16177F-01	-0.10334E	01 0.12156E	00 0.16670E	00 0.18937F-04 0.61400E 03
5	-0.15708E-01	-0.99983E	00 0.12144E	00 0.16711E	00 0.18934E-04 0.65900E 03
6	-0.15012E-01	-0.96668E	00 0.12143E	00 0.16720E	00 0.18932F-04 0.72300E 03
7	-0.14774F-01	-0.95535E	00 0.12143E	00 0.16722E	00 0.18932E-04 0.86200E 03
8	-0.14773F-01	-0.95534E	00 0.12142E	00 0.16722E	00 0.18932F-04 0.97900E 03

Table 3.... Cont'd

DEVIATION	CAL FUNC VALUE	OBS FUNC VALUE	REACTION TIME
0.103584E-02	0.144342E-01	0.154700E-01	0.100000E 01
-0.209865E-02	0.263086E-01	0.242100E-01	0.150000E 01
0.516757E-03	0.269732E-01	0.374900E-01	0.200000E 01
-0.570856E-03	0.466409E-01	0.460700E-01	0.250000E 01
-0.139001E-02	0.554290E-01	0.540300E-01	0.300000E 01
0.624193E-03	0.634058E-01	0.640399E-01	0.350000E 01
0.793296E-02	0.706170E-01	0.785500E-01	0.400000E 01
-0.181193E-03	0.771012E-01	0.769200E-01	0.450000E 01
-0.235730E-02	0.828972E-01	0.805399E-01	0.500000E 01
0.322288E-02	0.880471E-01	0.912700E-01	0.550000E 01
-0.996643E-02	0.925964E-01	0.826300E-01	0.600000E 01
-0.126374E-02	0.965937E-01	0.953300E-01	0.650000E 01
0.198114E-02	0.100089E 00	0.102070E 00	0.700000E 01
0.583369E-02	0.103131E 00	0.108970E 00	0.750000E 01
-0.123942E-02	0.105769E 00	0.104530E 00	0.800000E 01
-0.264901E-02	0.108049E 00	0.105400E 00	0.850000E 01
-0.200209E-02	0.110013E 00	0.107020E 00	0.900000E 01
-0.201046E-02	0.111700E 00	0.109690E 00	0.950000E 01
0.601280E-02	0.113147E 00	0.119160E 00	0.100000E 02

K1=-0.01477 K2=-0.95534 K3= 0.12142 K4= 0.16722 VARIANCE=0.90001893

TABLE 4

LEAST SQUARES 2 ORDER POLYNOMIALS

THE COEFFICIENTS OF THE FITTED FUNCTION ARE

A0 = -0.00484517

A1 = 0.02312628

A2 = -0.00114499

REGENERATED DATA

X MEASURED	Y OBSERVED	Y CALCULATED	PCT ERROR
1.000000	0.015470	0.017136	-10.769908
1.500000	0.024210	0.027268	-12.631151
2.000000	0.037490	0.036827	1.767411
2.500000	0.046070	0.045814	0.555033
3.000000	0.054030	0.054228	-0.367757
3.500000	0.064040	0.062070	3.075261
4.000000	0.078550	0.069340	11.725026
4.500000	0.076920	0.076036	1.148060
5.000000	0.080540	0.082161	-2.013082
5.500000	0.091270	0.087713	3.896979
6.000000	0.082630	0.092692	-12.177947
6.500000	0.095330	0.097099	-1.856213
7.000000	0.102070	0.100933	1.112996
7.500000	0.108970	0.104195	4.381109
8.000001	0.104530	0.106885	-2.253236
8.500001	0.105400	0.109002	-3.417682
9.000001	0.107020	0.110546	-3.295340
9.500001	0.109690	0.111518	-1.667031
10.000001	0.119160	0.111918	6.077538

VARIANCE = 0.000020

STANDARD DEVIATION = 0.004559

MAXIMUM PCT ERROR = 12.631151

TABLE 5

LEAST SQUARES 3 ORDER POLYNOMIALS

THE COEFFICIENTS OF THE FITTED FUNCTION ARE

A0 = -0.01571867
A1 = 0.03722293
A2 = -0.00308672
A3 = 0.00011768

REGENERATED DATA

X MEASURED	Y OBSERVED	Y CALCULATED	PCT ERROR
1.000000	0.015470	0.013535	12.506682
1.500000	0.024210	0.026067	-7.673576
2.000000	0.037490	0.037321	0.448803
2.500000	0.046070	0.047385	-2.855237
3.000000	0.054030	0.056347	-4.288366
3.500000	0.064040	0.064294	-0.397868
4.000000	0.078550	0.071317	9.208065
4.500000	0.076920	0.077502	-0.756701
5.000000	0.080540	0.082938	-2.977439
5.500000	0.091270	0.087713	3.896979
6.000000	0.082630	0.091915	-11.237981
6.500000	0.095330	0.095634	-0.319344
7.000000	0.102070	0.098956	3.049914
7.500000	0.108970	0.101971	6.422187
8.000001	0.104530	0.104767	-0.226817
8.500001	0.105400	0.107431	-1.927155
9.000001	0.107020	0.110052	-2.833504
9.500001	0.109690	0.112719	-2.761409
10.000001	0.119160	0.115519	3.055488

VARIANCE = 0.000017

STANDARD DEVIATION = 0.004212

MAXIMUM PCT ERROR = 12.506682

TABLE 6

LEAST SQUARES 4 ORDER POLYNOMIALS

THE COEFFICIENTS OF THE FITTED FUNCTION ARE

A0 = -0.01006018
A1 = 0.02543355
A2 = -0.00066513
A3 = -0.00021039
A4 = 0.00001491

REGENERATED DATA

X MEASURED	Y OBSERVED	Y CALCULATED	PCT ERROR
1.000000	0.015470	0.014512	6.187763
1.500000	0.024210	0.025959	-7.224295
2.000000	0.037490	0.036701	2.102340
2.500000	0.046070	0.046661	-1.284421
3.000000	0.054030	0.055781	-3.241837
3.500000	0.064040	0.064026	0.020988
4.000000	0.078550	0.071384	9.122414
4.500000	0.076920	0.077864	-1.228435
5.000000	0.080540	0.083500	-3.675873
5.500000	0.091270	0.088346	3.203693
6.000000	0.082630	0.092478	-11.918605
6.500000	0.095330	0.095997	-0.699696
7.000000	0.102070	0.099023	2.984320
7.500000	0.108970	0.101703	6.668657
8.000001	0.104530	0.104201	0.314459
8.500001	0.105400	0.106707	-1.240302
9.000001	0.107020	0.109432	-2.254180
9.500001	0.109690	0.112610	-2.662375
10.000001	0.119160	0.116497	2.234636

VARIANCE = 0.000018

STANDARD DEVIATION = 0.004312

MAXIMUM PCT ERROR = 11.918605

TABLE 7
COMPARISON OF DIFFERENT METHODS OF SMOOTHING SIMULATED DATA*

X=T(I)	SIMULATED DATA	TRUE VALUE	PRESENT METHOD	VALUES OF Y=F(T(I))** AFTER SMOOTHING LINEAR LEAST SQUARES POLY.			
				2ND	3RD	4TH	
1.00000	0.01547	0.01486	0.01443	0.01713	0.01353	0.01451	
1.50000	0.02421	0.02569	0.02630	0.02727	0.02606	0.02595	
2.00000	0.03749	0.03636	0.03697	0.03684	0.03728	0.03670	
2.50000	0.04607	0.04638	0.04664	0.04583	0.04730	0.04666	
3.00000	0.05403	0.05555	0.05542	0.05425	0.05619	0.05578	
3.50000	0.06404	0.06383	0.06340	0.06211	0.06404	0.06402	
4.00000	0.07855	0.07122	0.07061	0.06940	0.07093	0.07138	
4.50000	0.07692	0.07779	0.07709	0.07611	0.07693	0.07786	
5.00000	0.08054	0.08360	0.08289	0.08225	0.08213	0.08349	
5.50000	0.09127	0.08873	0.08804	0.08783	0.08663	0.08834	
6.00000	0.08263	0.09325	0.09259	0.09283	0.09048	0.09247	
6.50000	0.09533	0.09722	0.09659	0.09727	0.09379	0.09599	
7.00000	0.10207	0.10071	0.10008	0.10113	0.09664	0.09901	
7.50000	0.10897	0.10378	0.10312	0.10443	0.09909	0.10169	
8.00000	0.10453	0.10648	0.10576	0.10715	0.10124	0.10419	
8.50000	0.10540	0.10885	0.10804	0.10931	0.10313	0.10669	
9.00000	0.10702	0.11094	0.11000	0.11089	0.10497	0.10941	
9.50000	0.10969	0.11278	0.11169	0.11191	0.10672	0.11259	
10.00000	0.11916	0.11440	0.11314	0.11236	0.10848	0.11647	

* NORMALLY DISTRIBUTED 10 PER CENT ERROR RANDOMIZED BY SIGN,
WITHIN 95 PER CENT CONFIDENT LEVEL

** UNKNOWN FUNCTIONAL RELATIONSHIP

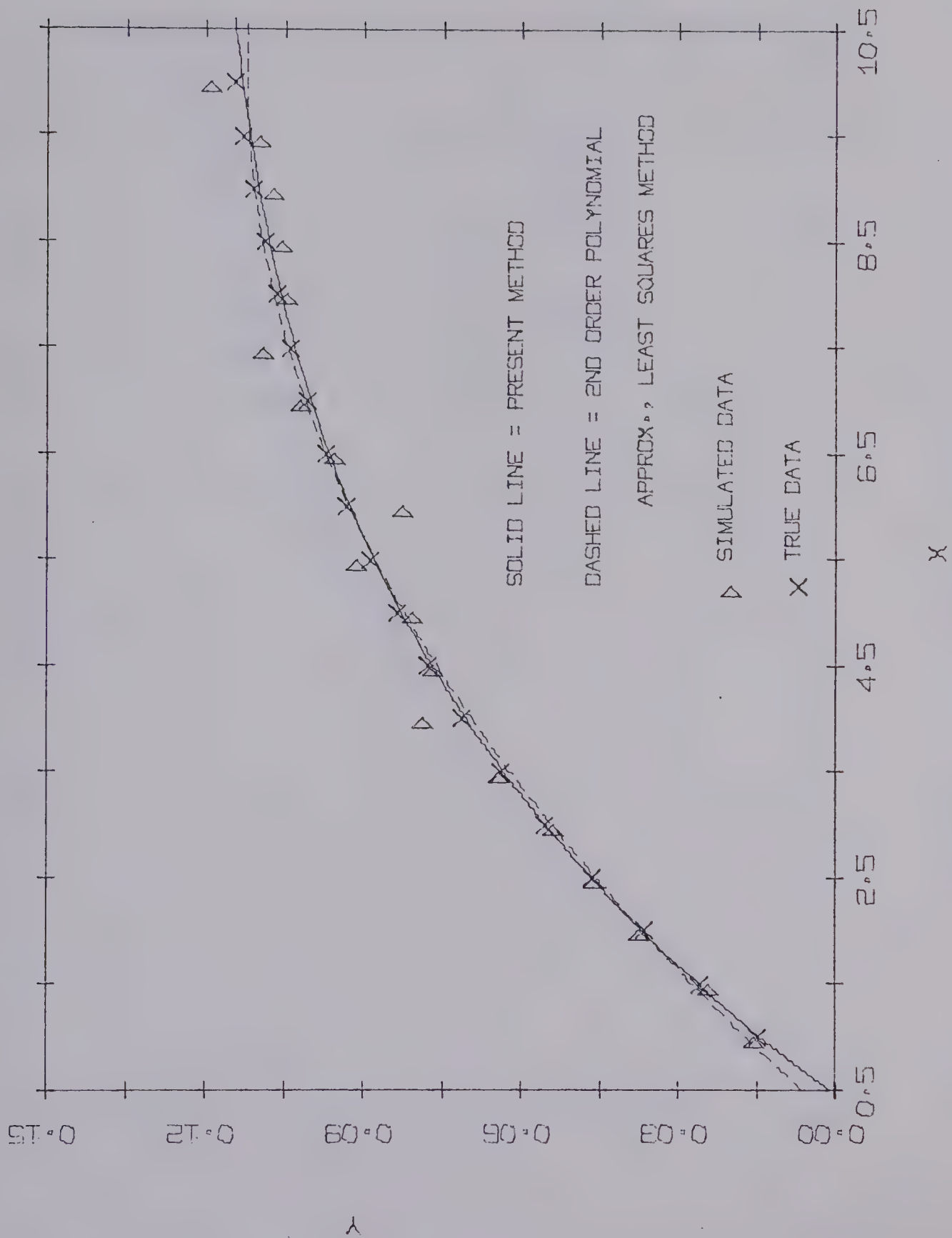


Figure 15 LINEAR LEAST SQUARES AND THE PRESENT METHOD

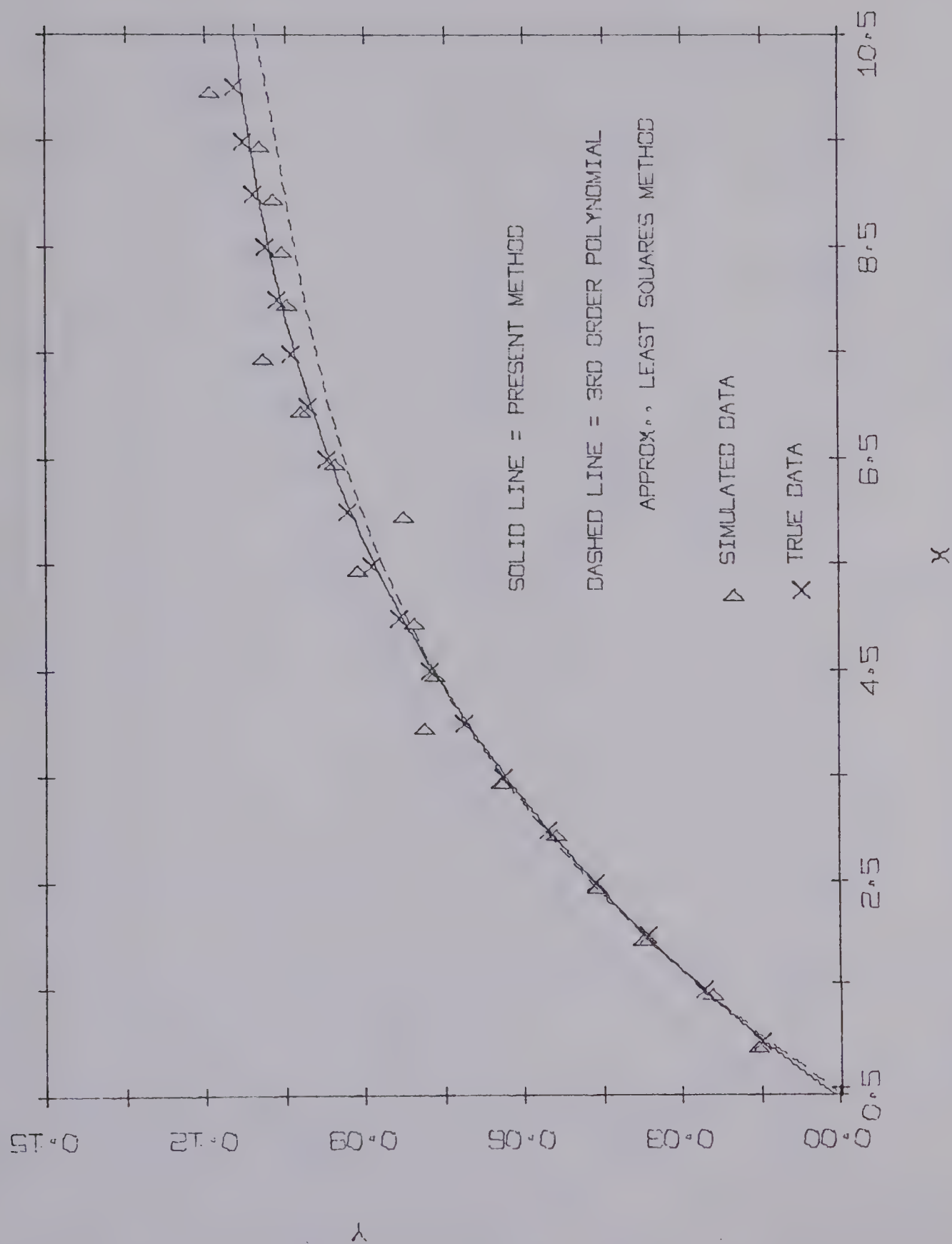


Figure 16 LINEAR LEAST SQUARES AND THE PRESENT METHOD

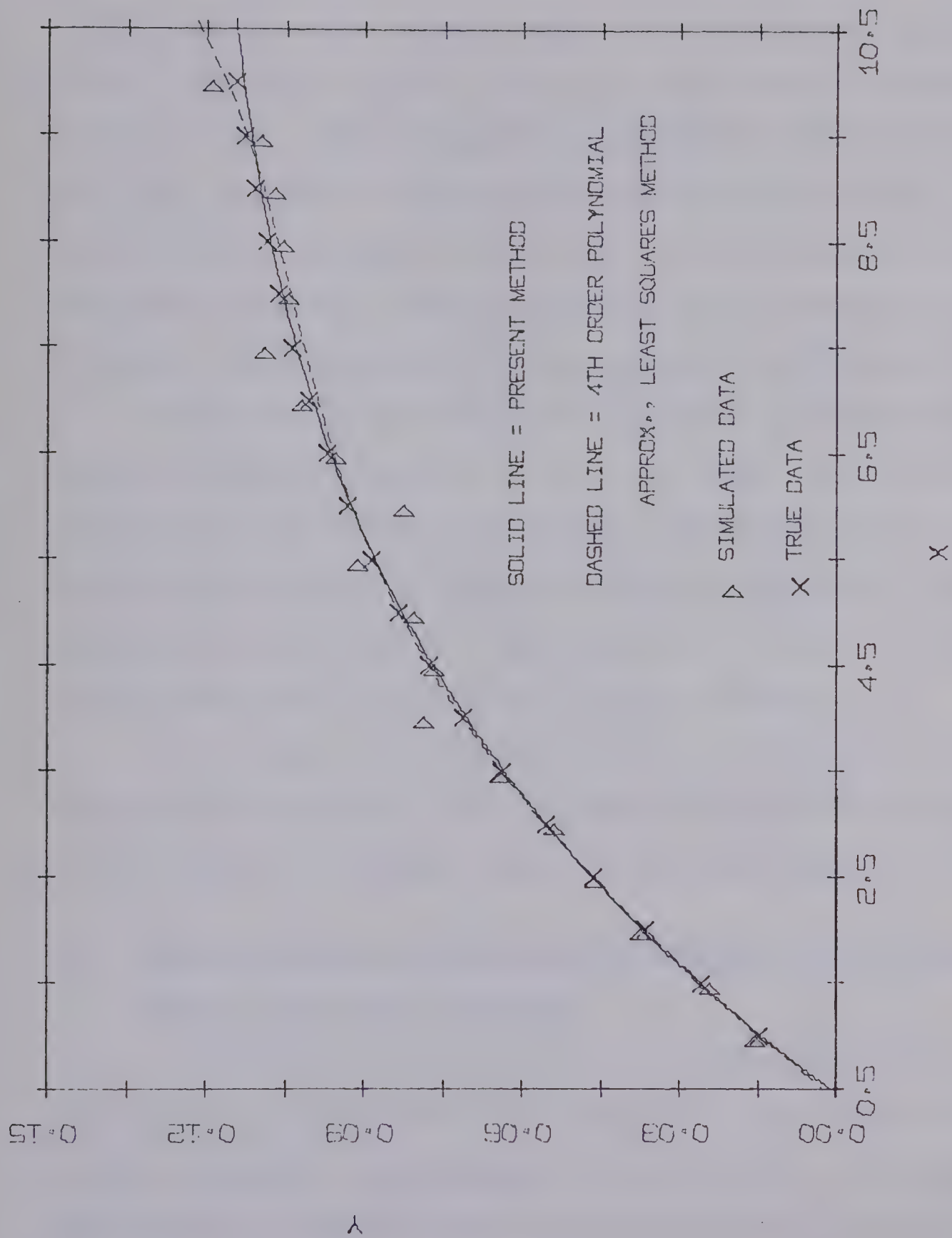


Figure 17 LINEAR LEAST SQUARES AND THE PRESENT METHOD

true and simulated values can be seen in Figure 15,16, and 17.

The error caused by second order polynomial-fitting in the vicinity of the origin are quite significant, although the approximation tends to approach to the true values at a distant from the origin. Third and fourth order polynomials approximate the data fairly well near the origin but deviate considerably as reaction time increases. The first derivatives obtained from the above four approximations were also tabulated in Table 8 to show how the error, which originated from smoothing, can be magnified through the process of differentiation.

The fact that the least-squares-polynomial approximations do not smooth the data accurately may be due to the defect that the polynomial employed does not satisfy the non-linear properties of the data. Thus, the resulting polynomial, obtained by using the criterion of sum-of-the-least-squares, may serve as an approximation to the function but not as a first derivative, as pointed out by Ralston (section 3.1.).

As a result, the method (3.5.) is more useful when accurate first derivatives are required. This is shown more clearly when the results of analyzing the hypothetical model are considered subsequently.

4.4. Analysis of Kinetic Model using Differentiation Technique and Method of Non-linear Estimation

The simulated concentration data, with 6% normally distributed random error at 95% confidence level around the exact values μ in Table 2, were regarded as the experimental data to be used in this example. The data will be differentiated (as per section 3.5.) and fitted by non-linear estimation.

TABLE 8
FIRST DERIVATIVES OF $Y=F(X)$
LINEAR LEAST SQUARES POLY.

X	PRESENT METHOD	2ND	3RD	4TH
1.00000	0.02517	0.02122	0.02639	0.02353
1.50000	0.02245	0.01888	0.02372	0.02221
2.00000	0.02026	0.01671	0.02122	0.02072
2.50000	0.01844	0.01470	0.01888	0.01909
3.00000	0.01674	0.01286	0.01671	0.01737
3.50000	0.01519	0.01118	0.01470	0.01560
4.00000	0.01364	0.00967	0.01286	0.01383
4.50000	0.01230	0.00832	0.01118	0.01210
5.00000	0.01090	0.00714	0.00967	0.01045
5.50000	0.00971	0.00612	0.00832	0.00894
6.00000	0.00852	0.00527	0.00714	0.00761
6.50000	0.00751	0.00458	0.00612	0.00649
7.00000	0.00652	0.00406	0.00527	0.00565
7.50000	0.00572	0.00370	0.00458	0.00511
8.00000	0.00491	0.00351	0.00406	0.00493
8.50000	0.00423	0.00348	0.00370	0.00515
9.00000	0.00363	0.00362	0.00351	0.00581
9.50000	0.00318	0.00146	0.00348	0.00696
10.00000	0.00274	0.00032	0.00362	0.00865

4.4.1. Computational Procedure

STEP 1. Smoothing Time-Composition Data

At the beginning of this step, it is generally useful to plot the time-composition data on graph paper, treating time as abscissa and composition as ordinate. Visual examination of such plots will give some guidance in selecting simulating functions for each reacting component (see Appendices 1 and 2 and references [11,22]).

The function which has a shape similar to that of the respective reacting component is fitted to the data. The parameters present in the fitted function are determined by minimizing the difference between calculated and true values of the concentration using Rosenbrock's Hill-Climbing method. The computer program was written in a format such that four different functions could be fitted to the same set of time-composition data during a single run of the program. Descriptions of read-in statements, input-data and their corresponding format are provided in Appendix 3.

To select the function which best fitted the set of time-composition data, the variance calculated for each fitting is examined and contrasted in Table 9.

Data at low concentrations are relatively more difficult to smooth accurately than data at high concentrations. Nevertheless, a reasonable accurate fit can be achieved when enough data are available. Reacting components, A_2 , A_3 , A_4 , and A_5 serve as good examples; 19 data points were employed. The results of the hill-climbing search for the best parameters by Rosenbrock's method are shown in Table 10, 11, 12, 13, 14, and 15. The initial guesses used in the iterative hill-climbing search operations, in all cases, were unity.

Table 9

Various smoothing functions for each reacting component

Reacting Component	No. of fit	Function fitted	Variance
A_1	1.	$-0.868e^{(0.253T)} + 1.34e^{(-0.253T)}$	0.676×10^{-3}
	*2.	$0.784/(0.755 + 1.102T)$	0.242×10^{-4}
A_2	1.	$T/[-266.9 + 271.2ATAN(T)^{0.008} + .64T^{2.54}]$	0.368×10^{-4}
	*2.	$T/[-12.127 + 5.003e^{(-.33T)} + 8.93e^{(.35T)}]$	0.226×10^{-4}
A_3	1.	$0.061ATAN(T)^{1.023}$	0.493×10^{-4}
	2.	$0.124TANH(0.159T)$	0.980×10^{-5}
	*3.	$-0.013e^{(-0.877T)} + 0.121TANH(0.167T)$	0.695×10^{-5}
A_4	1.	$T/[34.15 + 7.78e^{(.27T)} + .466^{(.27T)}]$	0.101×10^{-4}
	*2.	$T/[29.96 + 17.51ATAN(T)^{-1.71} + 0.851T^{2.117}]$	0.487×10^{-5}
A_5	1.	$-0.115T + 10^{(-0.106T)} - 1.98e^{(-0.149T)} + e^{(0.274T)}$	0.117×10^{-4}
	2.	$0.161e^{(0.069T)} - 0.177 \times 10^{(-0.017T)}$	0.115×10^{-4}
	*3.	$0.013T^{1.193} - 0.006T^{0.26}$	0.947×10^{-5}

* function chosen

T independent variable, reaction time

.. Table 10

A1 COMPONENT

$$\text{FUNCTION} = K1 / (K2 + K3 * T)$$

PARAMETER ESTIMATES BY ROSENBRACK METHOD

1	0.95000E	00	0.14000E	01	0.11000E	01	0.29242E-03	0.80000E	01
2	0.91165E	00	0.13068E	01	0.11015E	01	0.23963E-03	0.25000E	02
3	0.78440E	00	0.75532E	00	0.11029E	01	0.24190E-04	0.26300E	03
4	0.78448E	00	0.75531E	00	0.11029E	01	0.24190E-04	0.33500E	03

DEVIATION	CAL FUNC VALUE	OBS FUNC VALUE	REACTION TIME
-0.615434E-02	0.422175E 00	0.416020E 00	0.100000E 01
0.129302E-01	0.325561E 00	0.338509E 00	0.150000E 01
-0.106150E-02	0.264932E 00	0.262970E 00	0.200000E 01
0.342093E-02	0.223339E 00	0.226760E 00	0.250000E 01
-0.120415E-02	0.193034E 00	0.191640E 00	0.300000E 01
-0.930727E-03	0.169971E 00	0.169040E 00	0.350000E 01
-0.300023E-02	0.151830E 00	0.147939E 00	0.400000E 01
-0.612855E-02	0.137188E 00	0.131060E 00	0.450000E 01
-0.488240E-02	0.125122E 00	0.120240E 00	0.500000E 01
-0.268714E-02	0.115007E 00	0.111320E 00	0.550000E 01
0.489497E-02	0.106405E 00	0.111300E 00	0.600000E 01
0.321978E-02	0.990002E-01	0.102220E 00	0.650000E 01
0.100097E-02	0.925590E-01	0.944600E-01	0.700000E 01
-0.115472E-02	0.869047E-01	0.857500E-01	0.750000E 01
0.126856E-02	0.819014E-01	0.838700E-01	0.800000E 01
0.125700E-02	0.774420E-01	0.786999E-01	0.850000E 01
0.715196E-03	0.734448E-01	0.741600E-01	0.900000E 01
-0.127023E-02	0.698392E-01	0.685599E-01	0.950000E 01
-0.145108E-02	0.665711E-01	0.651200E-01	0.100000E 02

Table 11

*** A2 COMPONENT

$$\text{FUNCTION} = 1 / (K1 + K2 * \text{EXP}(K3 * T) + K4 * \text{EXP}(K5 * T))$$

PARAMETER ESTIMATES BY ROSENBRACK METHOD

ROTATION NO.	K1	K2	K3	K4	K5	VARIANCE	COUNT
1	0.25000E 00	0.80000E 00	0.80000E 00	0.80000E 00	0.80000E 00	0.26364E-02	0.21000E 02
2	0.16804E 01	0.80700E 00	0.64126E 00	0.69946E 00	0.70251E 00	0.10745E-02	0.32300E 03
3	0.35807E 00	0.11551E 01	0.57590E 00	0.11789E 01	0.59008E 00	0.59309E-03	0.52200E 04
4	0.37960E 01	0.22687E 01	0.32267E 00	0.30625E 01	0.47768E 00	0.71731E-04	0.55330E 04
5	0.40150E 01	0.24255E 01	0.16380E 00	0.44260E 01	0.43773E 00	0.47422E-04	0.50100E 04
6	0.62028E 01	0.20409E 01	0.14123E 00	0.46730E 01	0.43130E 00	0.45451E-04	0.60400E 04
7	0.75474E 01	0.33882E 01	0.55692E-01	0.54587E 01	0.41543E 00	0.42125E-04	0.60750E 04
8	0.90775E 01	0.38423E 01	0.64556E-01	0.65658E 01	0.39293E 00	0.34202E-04	0.61080E 04
9	0.10174E 02	0.42196E 01	0.15522E 00	0.74180E 01	0.37792E 00	0.28151E-04	0.61430E 04
10	0.11800E 02	0.47777E 01	0.29842E 00	0.87297E 01	0.35692E 00	0.23006E-04	0.64400E 04
11	0.11659E 02	0.47978E 01	0.30370E 00	0.87709E 01	0.35628E 00	0.22957E-04	0.65420E 04
12	0.11000E 02	0.44446E 01	0.31622E 00	0.98589E 01	0.35509E 00	0.22263E-04	0.65800E 04
13	0.11004E 02	0.44679E 01	0.22157E 00	0.88823E 01	0.35477E 00	0.22706E-04	0.66920E 04
14	0.10044E 02	0.44075E 01	0.32802E 00	0.89170E 01	0.35454E 00	0.22742E-04	0.70480E 04
15	0.12673E 02	0.43386E 01	0.33090E 00	0.89255E 01	0.35444E 00	0.22710E-04	0.71830E 04
16	0.12110E 02	0.44920E 01	0.33210E 00	0.89322E 01	0.35440E 00	0.22779E-04	0.73000E 04
17	0.11127E 02	0.50021E 01	0.33259E 00	0.89350E 01	0.35451E 00	0.22675E-04	0.74000E 04
18	0.11000E 02	0.50000E 01	0.33259E 00	0.89349E 01	0.35451E 00	0.22675E-04	0.77100E 04

Table 11 Cont'd

DEVIATION	CAL FUNC VALUE	CPS FUNC VALUE	REACTION TIME
-0.113770E-01	0.238257E-00	0.226380E-00	0.100000E-01
0.432553E-02	0.245194E-00	0.253530E-00	0.150000E-01
-0.163305E-02	0.232524E-00	0.230340E-00	0.200000E-01
0.421766E-02	0.213162E-00	0.217980E-00	0.250000E-01
0.921011E-03	0.192229E-00	0.193250E-00	0.300000E-01
0.146907E-02	0.172119E-00	0.173580E-00	0.350000E-01
-0.192729E-02	0.153327E-00	0.151400E-00	0.400000E-01
-0.464375E-02	0.136199E-00	0.131550E-00	0.450000E-01
-0.233227E-02	0.120742E-00	0.116860E-00	0.500000E-01
-0.214031E-02	0.106871E-00	0.103730E-00	0.550000E-01
0.418906E-02	0.944619E-01	0.986500E-01	0.600000E-01
0.223404E-02	0.833851E-01	0.856200E-01	0.650000E-01
0.350757E-03	0.735132E-01	0.743700E-01	0.700000E-01
-0.152767E-02	0.647277E-01	0.632000E-01	0.750000E-01
0.740658E-03	0.569193E-01	0.576600E-01	0.800000E-01
0.351038E-03	0.499300E-01	0.503400E-01	0.850000E-01
0.103715E-02	0.438463E-01	0.440400E-01	0.900000E-01
-0.66404E-03	0.384095E-01	0.377400E-01	0.950000E-01
-0.424512E-03	0.336045E-01	0.331800E-01	0.100000E-02

<1=-12.1270 K2= 5.00306 K3=-0.33259 K4= 8.93494 K5= 0.35451 VARIANCE=0.00002257

TABLE 12

*** A3 COMPONENT
FUNCTION = $K1 \cdot \tanh(K2 \cdot T)$
PARAMETER ESTIMATED BY ROSENBROCK METHOD

ROTAT. NO.	K1	K2	VARIANCE	COUNT
1	0.35000E 00	0.35000E 00	0.64334E-01	10
2	0.20190E 00	0.74630E-01	0.98170E-04	198
3	0.19427E 00	0.80231E-01	0.91023E-04	262
4	0.16135E 00	0.99732E-01	0.59910E-04	281
5	0.15013E 00	0.11009E 00	0.46901E-04	300
6	0.13800E 00	0.12703E 00	0.26418E-04	313
7	0.13320E 00	0.13593E 00	0.18726E-04	330
8	0.11866E 00	0.17442E 00	0.12640E-04	343
9	0.12411E 00	0.15945E 00	0.98051E-05	422
10	0.12413E 00	0.15942E 00	0.98050E-05	495
11	0.12413E 00	0.15942E 00	0.98050E-05	548

DEVIATION	CAL FUNC VALUE	OBS FUNC VALUE	REACTION TIME
0.440284E-02	0.196228E-01	0.152200E-01	0.100000E 01
0.433005E-02	0.291300E-01	0.248000E-01	0.150000E 01
0.124884E-02	0.382888E-01	0.370400E-01	0.200000E 01
0.818967E-03	0.470089E-01	0.461900E-01	0.250000E 01
0.579096E-03	0.552191E-01	0.546400E-01	0.300000E 01
-0.109191E-02	0.628681E-01	0.639600E-01	0.350000E 01
-0.569537E-02	0.699246E-01	0.756200E-01	0.400000E 01
-0.894054E-03	0.763759E-01	0.772700E-01	0.450000E 01
0.465244E-03	0.822252E-01	0.817600E-01	0.500000E 01
-0.276099E-02	0.874890E-01	0.902500E-01	0.550000E 01
0.531388E-02	0.921939E-01	0.868800E-01	0.600000E 01
0.293895E-03	0.963739E-01	0.960800E-01	0.650000E 01
-0.145234E-02	0.100067E 00	0.101520E 00	0.700000E 01
-0.357376E-02	0.103316E 00	0.106890E 00	0.750000E 01
0.861391E-03	0.106161E 00	0.105300E 00	0.800000E 01
0.186410E-02	0.108644E 00	0.106780E 00	0.850000E 01
0.221364E-02	0.110803E 00	0.108590E 00	0.900000E 01
0.175683E-02	0.112676E 00	0.110920E 00	0.950000E 01
-0.295224E-02	0.114297E 00	0.117250E 00	0.100000E 02

K1=0.12413 K2=0.15942 VARIANCE=0.00000980

Table 13

*** A3 COMPONENT

$$\text{FUNCTION} = K1 * \exp(K2 * T) + K3 * \tanh(K4 * T)$$

PARAMETER ESTIMATES BY ROSENBRROCK METHOD

ROTATION NO.	K1	K2	K3	K4	VARIANCE	COUNT
1	-0.15000E 00	-0.15000E 00	0.30000E 00	0.30000E 00	0.16685E-01	0.18000E 02
2	-0.93420E-01	-0.65060E-02	0.22832E 00	0.21513E 00	0.77892E-03	0.83000E 02
3	-0.37007E-02	0.17203E 00	0.14880E 00	0.14355E 00	0.91194E-05	0.17000E 04
4	-0.36205E-02	0.17207E 00	0.14882E 00	0.14351E 00	0.91164E-05	0.20000E 04
5	-0.32173E-02	0.17310E 00	0.14609E 00	0.14464E 00	0.90038E-05	0.22120E 04
6	-0.24722E-02	0.17473E 00	0.14086E 00	0.14801E 00	0.88886E-05	0.30000E 04
7	-0.24124E-02	0.17491E 00	0.14024E 00	0.14867E 00	0.88831E-05	0.33240E 04
8	-0.23907E-02	0.17492E 00	0.14010E 00	0.14884E 00	0.88926E-05	0.35250E 04
9	-0.23983E-02	0.17492E 00	0.14010E 00	0.14884E 00	0.88825E-05	0.36500E 04
10	-0.23428E-02	0.17453E 00	0.13970E 00	0.14866E 00	0.88783E-05	0.29510E 04
11	-0.23356E-02	0.17427E 00	0.13955E 00	0.14893E 00	0.88773E-05	0.40230E 04
12	-0.22937E-02	0.17403E 00	0.13942E 00	0.14905E 00	0.88742E-05	0.40020E 04
13	-0.21017E-02	0.17070E 00	0.13734E 00	0.15094E 00	0.88452E-05	0.42460E 04
14	-0.20425E-02	0.16910E 00	0.13668E 00	0.15151E 00	0.88390E-05	0.43050E 04
15	-0.20345E-02	0.16244E 00	0.13607E 00	0.15219E 00	0.87761E-05	0.50040E 04
16	-0.11222E-01	-0.69960E 00	0.12126E 00	0.16031E 00	0.60839E-05	0.50000E 04
17	-0.12595E-01	-0.77601E 00	0.12147E 00	0.16957E 00	0.60664E-05	0.50010E 04
18	-0.13769E-01	-0.87003E 00	0.12176E 00	0.16742E 00	0.69539E-05	0.63570E 04
19	-0.13003E-01	-0.87792E 00	0.12182E 00	0.16722E 00	0.69534E-05	0.66140E 04
20	-0.12303E-01	-0.87791E 00	0.12183E 00	0.16722E 00	0.69534E-05	0.66310E 04

Table 13 Cont'd

DEVIATION	CAL FUNC VALUE	GRS FUNC VALUE	REACTION TIME
-0.773057E-03	0.144459E-01	0.152200E-01	0.100000E 01
-0.143370E-02	0.262338E-01	0.248000E-01	0.150000E 01
0.135092E-03	0.360040E-01	0.370400E-01	0.200000E 01
-0.428867E-03	0.465189E-01	0.461900E-01	0.250000E 01
-0.825735E-03	0.554658E-01	0.546400E-01	0.300000E 01
0.459254E-03	0.635007E-01	0.639600E-01	0.350000E 01
0.485581E-02	0.707642E-01	0.756200E-01	0.400000E 01
-0.230670E-04	0.772330E-01	0.772700E-01	0.450000E 01
-0.136625E-02	0.831262E-01	0.817600E-01	0.500000E 01
0.104341E-02	0.883065E-01	0.902500E-01	0.550000E 01
-0.600082E-02	0.923800E-01	0.868800E-01	0.600000E 01
-0.812551E-03	0.968035E-01	0.960790E-01	0.650000E 01
0.110990E-02	0.100410E 00	0.101520E 00	0.700000E 01
0.342381E-02	0.103466E 00	0.106890E 00	0.750000E 01
-0.805371E-03	0.106115E 00	0.105310E 00	0.800000E 01
-0.162423E-02	0.108404E 00	0.106780E 00	0.850000E 01
-0.173581E-02	0.110376E 00	0.108590E 00	0.900000E 01
-0.114971E-02	0.112070E 00	0.110320E 00	0.950000E 01
0.372921E-02	0.113522E 00	0.117250E 00	0.100000E 02

K1=-0.01380 K2=-0.87791 K3= 0.12183 K4= 0.16722 VARIANCE= 0.00001

Table 14

*** A4 COMPONENT

FUNCTION = T/(K1*+K2*ACHTAN(T)**K3+K4*T**K5)

PARAMETER ESTIMATES BY ROSENBRACK METHOD

Rotation No.	K1	K2	K3	K4	K5	VARIANCE	COUNT
1	0.20044E	02 0.17487E	02-0.17154E	01 0.85124E	00 0.21165E	01 0.43514E-05	0.35770E 04
2	0.20000E	02 0.17503E	02-0.17151E	01 0.85128E	00 0.21171E	01 0.43736E-05	0.37770E 04
3	0.20070E	02 0.17515E	02-0.17149E	01 0.85124E	00 0.21176E	01 0.43731E-05	0.39170E 04
4	0.20000E	02 0.17514E	02-0.17149E	01 0.85124E	00 0.21176E	01 0.43731E-05	0.40260E 04

Table 14 Cont'd

DEVIATION	CAL FUNC VALUE	PBS FUNC VALUE	PF ACTION TIME
0.634745E-03	0.174452E-01	0.180900E-01	0.100000E 01
-0.130777E-02	0.209978E-01	0.225900E-01	0.150000E 01
0.133206E-03	0.413467E-01	0.414500E-01	0.200000E 01
-0.102013E-02	0.511402E-01	0.501200E-01	0.250000E 01
-0.170359E-02	0.592326E-01	0.574400E-01	0.300000E 01
-0.572244E-03	0.656293E-01	0.650499E-01	0.350000E 01
0.283007E-02	0.704260E-01	0.743099E-01	0.400000E 01
-0.344310E-03	0.737943E-01	0.732500E-01	0.450000E 01
-0.126427E-02	0.756342E-01	0.746700E-01	0.500000E 01
0.220527E-02	0.770546E-01	0.792600E-01	0.550000E 01
-0.413270E-02	0.773537E-01	0.732200E-01	0.600000E 01
0.581086E-03	0.770989E-01	0.775900E-01	0.650000E 01
0.222760E-02	0.761724E-01	0.784000E-01	0.700000E 01
0.375035E-02	0.740706E-01	0.787700E-01	0.750000E 01
0.393629E-03	0.735064E-01	0.739000E-01	0.800000E 01
-0.041108E-03	0.719611E-01	0.712200E-01	0.850000E 01
-0.142842E-02	0.700985E-01	0.686700E-01	0.900000E 01
-0.100704E-02	0.682679E-01	0.663600E-01	0.950000E 01
-0.216563E-03	0.664066E-01	0.661899E-01	0.100000E 02

- 68a -

K1=20.000375 K2=17.51378 K3=-1.71482 K4= 0.85124 K5= 2.11755 VARIATION=0.0000455

Table 15

*** A5 COMPONENT

FUNCTION = K1*T**K2+K3*T**K4

PARAMETER ESTIMATES BY POISENBPOCK METHOD

ROTATION NO.	K1	K2	K3	K4	VARIANCE	COUNT
1	0.12077E-01	0.11963E	01-0.69826E-02	0.26066E 00	0.94924E-05	0.10700E 03
2	0.12993E-01	0.11966E	01-0.69841E-02	0.26065E 00	0.94899E-05	0.36800E 03
3	0.13060E-01	0.11937E	01-0.69872E-02	0.26059E 00	0.94758E-05	0.63100E 03
4	0.13062E-01	0.11936E	01-0.69970E-02	0.26059E 00	0.94756E-05	0.66000E 03
5	0.12062E-01	0.11926E	01-0.69948E-02	0.26059E 00	0.94756E-05	0.73300E 03

Table 15 Cont'd

DEVIATION	CAL FUNC VALUE	CPS FUNC VALUE	REACTION TIME
0.746300E-04	0.606532E-02	0.614000E-02	0.100000E 01
-0.170631E-02	0.134162E-01	0.117100E-01	0.150000E 01
-0.140333E-02	0.214023E-01	0.200000E-01	0.200000E 01
-0.204850E-02	0.301066E-01	0.280600E-01	0.250000E 01
-0.226552E-02	0.391555E-01	0.368900E-01	0.300000E 01
-0.102500E-02	0.485651E-01	0.475400E-01	0.350000E 01
0.312150E-02	0.582884E-01	0.614200E-01	0.400000E 01
-0.189277E-03	0.682832E-01	0.681199E-01	0.450000E 01
-0.749830E-03	0.785396E-01	0.777900E-01	0.500000E 01
0.318325E-02	0.890167E-01	0.922000E-01	0.550000E 01
-0.403239E-02	0.997024E-01	0.948700E-01	0.600000E 01
0.113016E-02	0.110581E 00	0.111720E 00	0.650000E 01
0.257074E-02	0.121639E 00	0.125210E 00	0.700000E 01
0.651354E-02	0.132866E 00	0.139380E 00	0.750000E 01
0.447310E-03	0.144252E 00	0.144700E 00	0.800000E 01
-0.161839E-02	0.155788E 00	0.154170E 00	0.850000E 01
-0.317600E-02	0.167467E 00	0.164290E 00	0.900000E 01
-0.302116E-02	0.179231E 00	0.175400E 00	0.950000E 01
0.205267E-02	0.191225E 00	0.192310E 00	0.100000E 02

K1= 0.01306 K2= 1.19356 K3=-0.00700 K4= 0.26059 VARIANCE= 0.000000

In Table 9, the results of fitting component, A_3 , serve to show how one can build a function which smooths the data more accurately by building upon the knowledge obtained in the preceding trial. In the first fit for A_3 component as shown in Table 12, the function $k_1 \tanh(k_2 T)$ smooths the data reasonably accurate except for the first 4 or 5 points. By introducing an exponential term with two parameters to the previous function, the accuracy of the fit to the first 4 or 5 points improves considerably.

STEP 2 Material Balance Check

When all functions which smooth each of the reacting components were obtained, the concentration data were regenerated from the functions and the total concentration at a specific time was evaluated and compared with the initial value. If poor agreement resulted, then the reacting component with the largest variance is approximated again by adding more terms to the same function or by introducing a completely new function.

As a practical case, example 3 in the following chapter 5, will demonstrate how useful this criterion is, especially when the variance of the fit of two functions are about the same. For example 1, the material balance check was presented in Table 16. As can be seen, the total number of mole/litre thus obtained from the functions is about 1% more or less than that of the initial values. The accuracy here is well assured if one recognize the fact that any error introduced by the smooth function, will be magnified four times in the case of A_4 component, two times in the cases of A_2 , A_3 , and A_5 , during the process of material balance. This is so, because of the non-linear reaction system assumed for this example.

TABLE 16
EXAMPLE 1

REACTION TIME (HR.)	CONCENTRATION DATA REGENERATED FROM THE FITTED FUNCTIONS					MATERIAL* BALANCE
	A1	A2	A3	A4	A5	
1.00000	0.42217	0.23825	0.01444	0.01750	0.00606	1.00971
1.50000	0.32556	0.24519	0.02623	0.02951	0.01340	1.01330
2.00000	0.26493	0.23252	0.03690	0.04058	0.02148	1.00909
2.50000	0.22333	0.21316	0.04662	0.05034	0.03009	1.00049
3.00000	0.19303	0.19232	0.05546	0.05861	0.03914	1.00136
3.50000	0.16997	0.17211	0.06350	0.06529	0.04855	0.99950
4.00000	0.15183	0.15332	0.07076	0.07042	0.05827	0.99824
4.50000	0.13718	0.13619	0.07729	0.07408	0.06827	0.99706
5.00000	0.12512	0.12074	0.08312	0.07645	0.07851	0.99570
5.50000	0.11500	0.10686	0.08830	0.07770	0.08899	0.99417
6.00000	0.10640	0.09446	0.09288	0.07804	0.09967	0.99262
6.50000	0.09900	0.08338	0.09690	0.07765	0.11055	0.99128
7.00000	0.09255	0.07351	0.10041	0.07669	0.12161	0.99040
7.50000	0.08690	0.06472	0.10346	0.07531	0.13283	0.99021
8.00000	0.08190	0.05691	0.10611	0.07362	0.14422	0.99092
8.50000	0.07744	0.04998	0.10840	0.07173	0.15575	0.99267
9.00000	0.07344	0.04384	0.11037	0.06970	0.16743	0.99558
9.50000	0.06983	0.03840	0.11207	0.06760	0.17924	0.99971
10.00000	0.06657	0.03360	0.11352	0.06547	0.19118	1.00510

*TOTAL NUMBER OF MOLE/LITRE EQUIVALENT TO INITIAL VALUE OF COMPONENT,
A1, PRESENT IN THE REACTION SYSTEM AT A COMMON INSTANTANEOUS TIME =
 $A1 + 2*A2 + 2*A3 + 4*A4 + 2*A5$

TABLE 17

EXAMPLE 1

REACTION RATE OBTAINED BY DIRECT DIFFERENTIATION OF THE FITTED FUNCTIONS

REACTION TIME (HR.)	A1	A2	REACTION RATE A3	A4	A5	TOTAL RATE**
1.00000	-0.25057	0.04967	0.02484	0.02569	0.01376	0.02874
1.50000	-0.14900	-0.01211	0.02238	0.02408	0.01550	-0.00113
2.00000	-0.09867	-0.03460	0.02034	0.02121	0.01673	-0.00890
2.50000	-0.07012	-0.04123	0.01855	0.01791	0.01768	-0.00848
3.00000	-0.05238	-0.04145	0.01685	0.01448	0.01847	-0.00672
3.50000	-0.04061	-0.03914	0.01528	0.01114	0.01914	-0.00549
4.00000	-0.03240	-0.03594	0.01379	0.00813	0.01973	-0.00474
4.50000	-0.02645	-0.03256	0.01233	0.00545	0.02025	-0.00462
5.00000	-0.02200	-0.02929	0.01099	0.00321	0.02073	-0.00430
5.50000	-0.01859	-0.02623	0.00977	0.00137	0.02116	-0.00371
6.00000	-0.01591	-0.02344	0.00861	-0.00005	0.02156	-0.00265
6.50000	-0.01377	-0.02090	0.00753	-0.00125	0.02193	-0.00165
7.00000	-0.01204	-0.01861	0.00652	-0.00202	0.02228	0.00024
7.50000	-0.01061	-0.01655	0.00575	-0.00265	0.02261	0.00238
8.00000	-0.00943	-0.01470	0.00494	-0.00312	0.02292	0.00439
8.50000	-0.00843	-0.01304	0.00429	-0.00339	0.02321	0.00692
9.00000	-0.00758	-0.01155	0.00372	-0.00360	0.02349	0.00933
9.50000	-0.00685	-0.01021	0.00315	-0.00372	0.02375	0.01163
10.00000	-0.00623	-0.00902	0.00271	-0.00369	0.02400	0.01439

**THE SUM OF REACTION RATES FOR ALL COMPONENTS AT A COMMON INSTANTANEOUS
TIME = RA1 + 2*RA2 + 2*RA3 + 4*RA4 + 2RA5

STEP 3: Differentiation of the Function

The first derivatives of the smoothed function can be obtained simply by differentiating the fitted function analytically. If the function cannot be differentiated analytically, then the five-point formula of Whitaker [40] can be used for numerical differentiation. The procedure can be summarized as follow: generate five equal-spaced concentration data points from the fitted function, in such a way that the concentration data corresponding to a specific reaction time at which the first derivative is desired, is the middle point among the five points generated.

For example 1, the rate balance is shown in Table 17. The non-linearity of the reaction system still exists hence the accuracy of the total rate balance in Table 17 is well assured.

STEP 4: Computation of Reaction Step

From the theory developed in section (2.2.1.) the rate balance for each reacting component in the reaction system of Figure 14, can be written as:

$$\begin{aligned}r_1 &= -r_{11} \\r_2 &= r_{11/2} - r_{22} - r_{23} \\r_3 &= r_{22} \\r_4 &= r_{23/2} - r_{44} \\r_5 &= 2r_{44}\end{aligned}\tag{4-7}$$

Because the Left-Hand-Side terms of equation (4-7) are known from STEP 3, and since reaction steps r_{11} , r_{22} , and r_{44} are defined already, by substitution, reaction step r_{23} can be obtained either from the rate

balance for A_2 or A_4 components. Component A_2 , giving $r_2 = r_{11/2} - r_{22} - r_{23}$ was chosen because the higher concentration values available can eliminate some of the error originating with smoothing.

STEP 5 Simultaneous estimation of rate constant and order of reaction

Since the values of the concentrations of each reacting component and the rate values of each reaction steps at a specific reaction time, have been obtained it remains to find k_{ij} and n_{ij} from equation(4-8)

$$r_{ij} = k_{ij} C_i^{n_{ij}} \quad (4-8)$$

Because of the limited knowledge available on error variance of the experimental data, the logarithmic transformation approach suggested by Levenspiel [24] is not recommended here. Instead, the Rosenbrock Hill-Climbing method is utilized to fit the power function $k_{ij} C_i^{n_{ij}}$. The smooth values of concentration data, C_i' , calculated from the functions for each component A_i were employed in this step. The results for each reaction step were presented in the Tables 18, 19, 20, and 21.

In brief, the results may be summarized with the corresponding true values as shown below in Table 22.

Using the parameters obtained from these calculations, the reaction path is plotted against the simulated data. The agreement is within the experimental error even for the low concentration components, A_2 , A_3 , A_4 and A_5 . The complete plot of all five reacting components is shown on Figure 18. An enlarged plot for the low concentration range of component A_2 , A_3 , A_4 , and A_5 can be seen in Figure 19.

TABLE 18

SIMULTANEOUS ESTIMATING OF RATE CONSTANT AND ORDER OF
REACTION BY NON-LINEAR FITTING

EXAMPLE 1, REACTION STEP 11

RATE = RATE CONSTANT*CONC**ORDER

ROTAT. NO.	RATE CONSTANT	N-ORDER	VARIANCE	COUNT
1	0.800000E 00	0.140000E 01	0.435619E-03	7
5	0.124150E 01	0.188698E 01	0.810760E-05	93
10	0.130091E 01	0.192873E 01	0.314710E-05	204
15	0.131688E 01	0.193884E 01	0.229990E-05	301
20	0.133526E 01	0.195276E 01	0.136980E-05	412
25	0.135256E 01	0.196434E 01	0.775800E-06	517
30	0.140186E 01	0.199737E 01	0.460000E-08	631
31	0.140182E 01	0.199735E 01	0.460000E-08	677

DEVIATION	CALCULATED RATE	OBS RATE	CONC.
-0.155508E-03	0.250414E 00	0.250570E 00	0.422170E 00
0.204741E-04	0.149020E 00	0.149000E 00	0.325560E 00
0.677555E-04	0.987377E-01	0.986700E-01	0.264930E 00
0.759214E-04	0.701959E-01	0.701200E-01	0.223330E 00
0.808388E-04	0.524608E-01	0.523800E-01	0.193030E 00
0.789538E-04	0.406889E-01	0.406100E-01	0.169970E 00
0.770837E-04	0.324770E-01	0.324000E-01	0.151830E 00
0.691861E-04	0.265191E-01	0.264500E-01	0.137180E 00
0.667274E-04	0.220667E-01	0.220000E-01	0.125120E 00
0.556409E-04	0.186456E-01	0.185900E-01	0.115000E 00
0.544637E-04	0.159644E-01	0.159100E-01	0.106400E 00
0.537056E-04	0.138237E-01	0.137700E-01	0.990000E-01
0.432711E-04	0.120832E-01	0.120400E-01	0.925500E-01
0.447630E-04	0.106547E-01	0.106100E-01	0.869000E-01
0.354237E-04	0.946542E-02	0.943000E-02	0.819000E-01
0.338424E-04	0.846384E-02	0.843000E-02	0.774400E-01
0.331271E-04	0.761312E-02	0.758000E-02	0.734400E-01
0.339839E-04	0.688398E-02	0.685000E-02	0.698300E-01
0.270279E-04	0.625702E-02	0.623000E-02	0.665700E-01

RATE CONSTANT= 1.401820
ORDER OF REACTION=1.9973

Table 19

SIMULTANEOUS ESTIMATING OF RATE CONSTANT AND ORDER OF REACTION ,
BY NON-LINEAR FITTING

EXAMPLE 1, REACTION STEP 22

PATE = RATE CONSTANT*CONC**ORDER

POTATION NO.	RATE CONSTANT	N-ORDER	VARIANCE	COUNT	
1	0.916540E-01	0.100415E 01	0.728594E-06	0.490000E 02	- .75 -
2	0.918082E-01	0.100424E 01	0.727972E-06	0.740000E 02	
3	0.917614E-01	0.100432E 01	0.727824E-06	0.116000E 03	
4	0.920106E-01	0.100488E 01	0.726649E-06	0.180000E 03	- .75 -
5	0.919515E-01	0.100497E 01	0.726190E-06	0.204000E 03	
6	0.919939E-01	0.100505E 01	0.726035E-06	0.228000E 03	
7	0.919152E-01	0.100507E 01	0.725921E-06	0.257000E 03	- .75 -
8	0.919885E-01	0.100523E 01	0.725543E-06	0.287000E 03	
9	0.919514E-01	0.100530E 01	0.725319E-06	0.356000E 03	
10	0.919833E-01	0.100546E 01	0.724948E-06	0.237000E 03	- .75 -
11	0.919571E-01	0.100547E 01	0.724940E-06	0.446000E 03	
12	0.920845E-01	0.100568E 01	0.724490E-06	0.482000E 03	
13	0.920536E-01	0.100574E 01	0.724266E-06	0.519000E 03	- .75 -
14	0.920243E-01	0.100606E 01	0.723587E-06	0.564000E 03	
15	0.938531E-01	0.101699E 01	0.700638E-06	0.228000E 04	
16	0.938250E-01	0.101701E 01	0.700621E-06	0.231200E 04	- .75 -
17	0.939052E-01	0.101717E 01	0.700395E-06	0.234200E 04	
18	0.938486E-01	0.101718E 01	0.700324E-06	0.237700E 04	
19	0.939221E-01	0.101733E 01	0.700078E-06	0.240700E 04	- .75 -
20	0.938855E-01	0.101743E 01	0.699870E-06	0.244800E 04	
21	0.938974E-01	0.101771E 01	0.699426E-06	0.249300E 04	
22	0.939322E-01	0.101774E 01	0.699236E-06	0.252700E 04	- .75 -
23	0.939294E-01	0.101772E 01	0.699336E-06	0.259000E 04	

Table 19 Cont'd

DEVIATION	CALCULATED RATE	OBS RATE	CONC.
-0.140863E-62	0.218170E-01	0.248400E-01	0.238250E-03
0.302298E-02	0.224640E-01	0.223800E-01	0.245197E-03
-0.839718E-04	0.212832E-01	0.203400E-01	0.232520E-03
-0.943154E-03	0.194811E-01	0.185500E-01	0.213160E-03
-0.931058E-03	0.175444E-01	0.168500E-01	0.192320E-03
-0.694425E-03	0.156699E-01	0.152800E-01	0.172110E-03
-0.389896E-03	0.139306E-01	0.137900E-01	0.153320E-03
-0.140585E-03	0.126223E-01	0.123300E-01	0.139160E-03
-0.292316E-03	0.109240E-01	0.109900E-01	0.120740E-03
0.659600E-04	0.964733E-02	0.977000E-02	0.106860E-03
0.122666E-03	0.850924E-02	0.861000E-02	0.944600E-03
0.100762E-03	0.749453E-02	0.753000E-02	0.833800E-03
0.354648E-04	0.659265E-02	0.652000E-02	0.735100E-03
-0.726465E-04	0.579124E-02	0.575000E-02	0.647200E-03
-0.412427E-04	0.508080E-02	0.494000E-02	0.569100E-03
-0.140797E-03	0.445185E-02	0.429000E-02	0.499800E-03
-0.161849E-03	0.389588E-02	0.372000E-02	0.438400E-03
-0.175884E-03	0.340445E-02	0.315000E-02	0.384000E-03
-0.254451E-03	0.297185E-02	0.271000E-02	0.336000E-03

RATE CONSTANT= 0.093929

N - ORDER OF REACTION=1.0177

Table 20

SIMULTANEOUS ESTIMATING OF RATE CONSTANT AND ORDER OF REACTION
BY NON-LINEAR FITTING

EXAMPLE 1, REACTION STEP 23

RATE = RATE CONSTANT*CONC**ORDER

ITERATION NO.	RATE CONSTANT	N-ORDER	VARIANCE	COUNT
1	0.251562E 00	0.996873E 00	0.872208E-05	0.150000E 02
2	0.251638E 00	0.996970E 00	0.872133E-05	0.400000E 02
3	0.251903E 00	0.997304E 00	0.871925E-05	0.790000E 02
4	0.251968E 00	0.997400E 00	0.871828E-05	0.100000E 03
5	0.252059E 00	0.998061E 00	0.871248E-05	0.131000E 03
6	0.252580E 00	0.999056E 00	0.870728E-05	0.180000E 03
7	0.252883E 00	0.999735E 00	0.870307E-05	0.182000E 03
8	0.252907E 00	0.999902E 00	0.870203E-05	0.210000E 03
9	0.252948E 00	0.100010E 01	0.870087E-05	0.300000E 03
10	0.252945E 00	0.100008E 01	0.870078E-05	0.381000E 03

Table 20 Cont'd

DEVIATION	CALCULATED RATE	Cont'd RHS RATE	CMC.
-0.942650E-02	0.602560E-01	0.597700E-01	0.233250E 00
0.00176E-02	0.620123E-01	0.642300E-01	0.245100E 00
0.472232E-02	0.589077E-01	0.635900E-01	0.232520E 00
0.332916E-02	0.529108E-01	0.577400E-01	0.213160E 00
0.015028E-02	0.496397E-01	0.507900E-01	0.192320E 00
0.632040E-02	0.435230E-01	0.441600E-01	0.172110E 00
-0.425462E-02	0.387755E-01	0.383500E-01	0.153320E 00
-0.174401E-02	0.351940E-01	0.334500E-01	0.139160E 00
-0.12351E-02	0.305352E-01	0.292000E-01	0.120740E 00
-0.12762E-02	0.270246E-01	0.257500E-01	0.106860E 00
-0.11034E-02	0.229884E-01	0.227800E-01	0.944600E-01
-0.036138E-02	0.210861E-01	0.202500E-01	0.833800E-01
-0.479914E-02	0.185899E-01	0.181100E-01	0.735100E-01
-0.266829E-02	0.163668E-01	0.161000E-01	0.647200E-01
0.782301E-02	0.143916E-01	0.144700E-01	0.569100E-01
0.320000E-02	0.126390E-01	0.129600E-01	0.499900E-01
0.533812E-02	0.110362E-01	0.116200E-01	0.439400E-01
0.762582E-02	0.971042E-02	0.104800E-01	0.384000E-01
0.923473E-02	0.849652E-02	0.942000E-02	0.336000E-01

RATE CONSTANT= 0.252945

N - ORDER OF REACTION=1.0001

TABLE 21

SIMULTANEOUS ESTIMATING OF RATE CONSTANT AND ORDER OF
REACTION BY NON-LINEAR FITTING

EXAMPLE 1, REACTION STEP 44

$$\text{RATE} = \text{RATE CONSTANT} * \text{CONC} ** \text{ORDER}$$

ROTAT. NO.	RATE CONSTANT	N-ORDER	VARIANCE	COUNT
1	0.618869E-01	0.398632E	00 0.251930E-05	37
5	0.610502E-01	0.398582E	00 0.251900E-05	198
10	0.618301E-01	0.398483E	00 0.251880E-05	388
15	0.617794E-01	0.398352E	00 0.251870E-05	588
20	0.617640E-01	0.398207E	00 0.251830E-05	796
25	0.617465E-01	0.398084E	00 0.251800E-05	967
30	0.617386E-01	0.398021E	00 0.251790E-05	1161
35	0.617307E-01	0.397855E	00 0.251780E-05	1346
40	0.617323E-01	0.397899E	00 0.251760E-05	1554
43	0.617197E-01	0.397875E	00 0.251760E-05	1708

DEVIATION	CALCULATED RATE	OBS RATE	CONC.
-0.143396E-02	0.123260E-01	0.137600E-01	0.174450E-01
-0.209242E-03	0.152907E-01	0.155000E-01	0.299870E-01
0.645335E-03	0.173753E-01	0.167300E-01	0.413460E-01
0.122898E-02	0.189089E-01	0.176800E-01	0.511400E-01
0.157721E-02	0.200472E-01	0.184700E-01	0.592330E-01
0.174188E-02	0.208818E-01	0.191400E-01	0.656280E-01
0.174643E-02	0.214764E-01	0.197300E-01	0.704260E-01
0.162933E-02	0.218793E-01	0.202500E-01	0.737939E-01
0.129962E-02	0.221296E-01	0.207300E-01	0.759340E-01
0.109846E-02	0.222584E-01	0.211600E-01	0.770500E-01
0.733245E-03	0.222932E-01	0.215600E-01	0.773530E-01
0.322714E-03	0.222527E-01	0.219300E-01	0.770000E-01
-0.122800E-03	0.221571E-01	0.222800E-01	0.761720E-01
0.324256E-01	0.550356E-01	0.226100E-01	0.749700E 00
-0.107466E-02	0.218453E-01	0.229200E-01	0.735060E-01
-0.156062E-02	0.216493E-01	0.232100E-01	0.718600E-01
-0.205341E-02	0.214365E-01	0.234900E-01	0.700980E-01
-0.253798E-02	0.212120E-01	0.237500E-01	0.682670E-01
-0.302072E-02	0.209792E-01	0.240000E-01	0.664000E-01

RATE CONSTANT= 0.061719
ORDER OF REACTION=0.3978

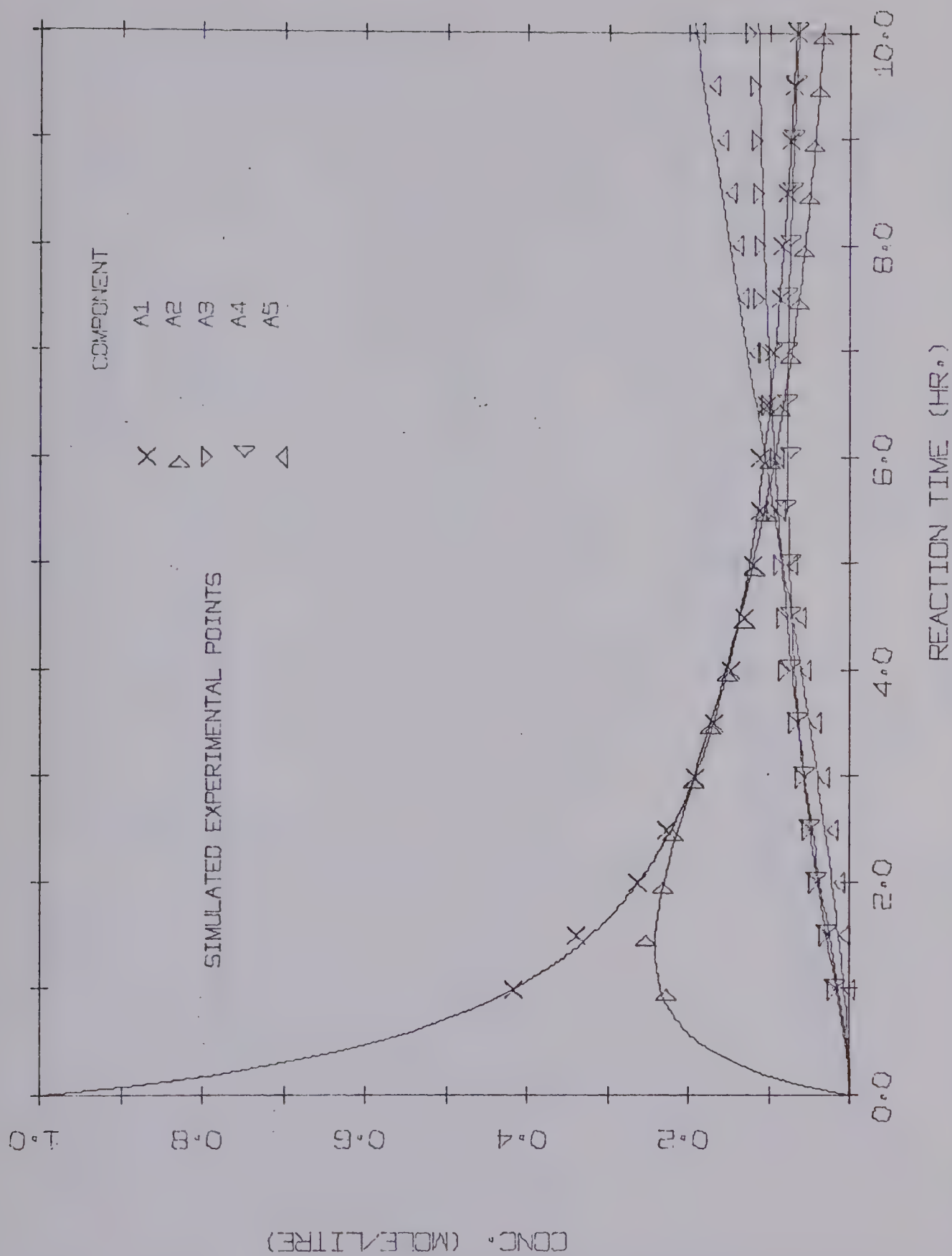


Figure 18 REACTION PATH CALCULATED FROM KINETIC MODEL OBTAINED FROM THIS WORK
HYPOTHETICAL REACTION SYSTEM, EXAMPLE NO. 1

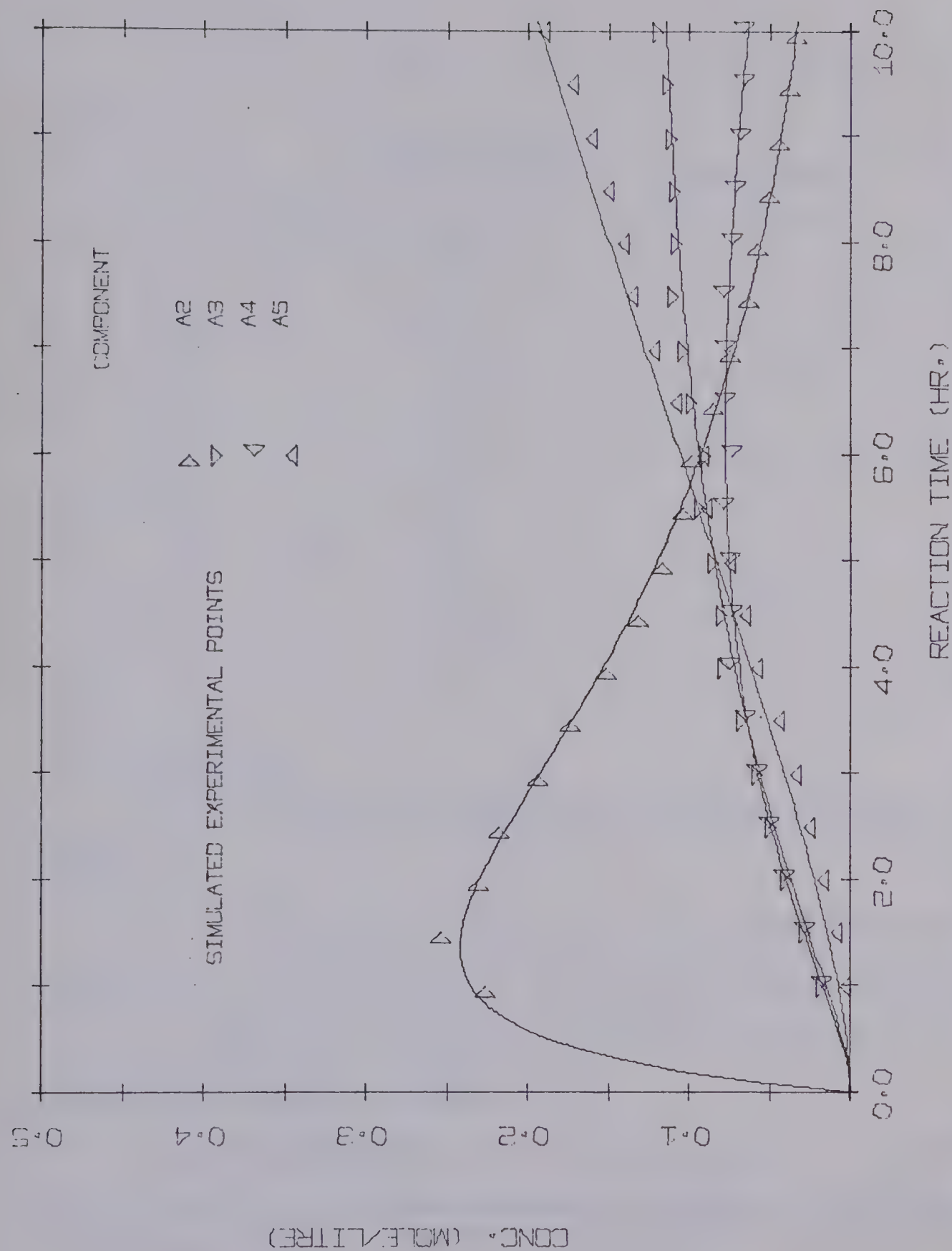


Figure 19 REACTION PATH CALCULATED FROM KINETIC MODEL OBTAINED FROM THIS WORK
HYPOTHETICAL REACTION SYSTEM, EXAMPLE NO. 1

TABLE 22

parameters	values obtained by this work	true values
k_{11}	1.401	1.4
n_{11}	1.997	2
k_{22}	0.094	0.09
n_{22}	1.017	1
k_{23}	0.252	0.25
n_{23}	1.000	1
k_{44}	0.031	0.04
n_{44}	0.398	0.5

4.5. Conclusions

From the results of example 1, the following conclusions may be drawn:

1. the smoothing technique used in this example gave accurate results and its applicability to other problems appears justified;
2. the method of analysis for multiple-step reaction systems successfully simulated example 1;
3. low concentrations of reacting components can be analyzed as accurately as the higher concentration components in the presence of enough data.

4.6. Testing Alternative Chemical Reaction-Step Models with Experimental Rate Data

In chemical kinetics research, it is always necessary for the investigator to check the adequacy of fit of the experimental rate data to alternative networks of reaction steps which appear to be feasible. The following sequential approach was used in this work to evaluate this problem. It relies mainly on two criteria: (1) physical realizability and, (2) statistical justification. The former criterion implies that the parameters cannot take values incompatible with those from nature, and the latter criterion rests on relative values of some statistical property such as the variance.

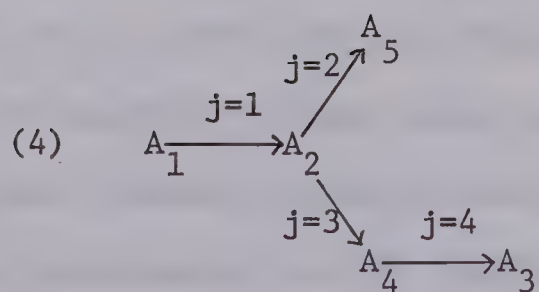
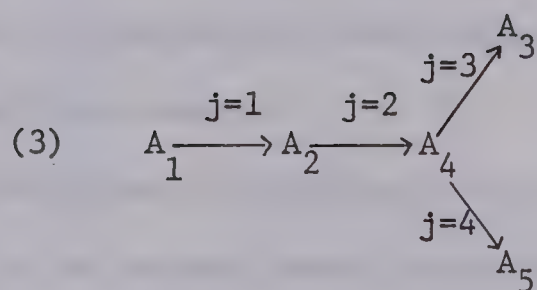
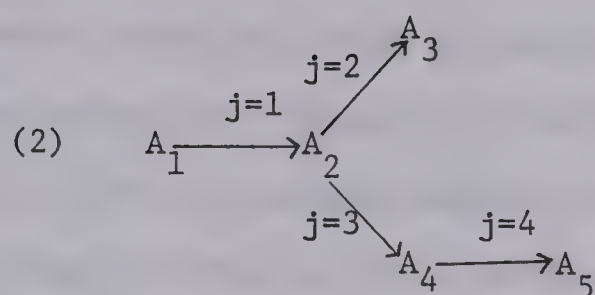
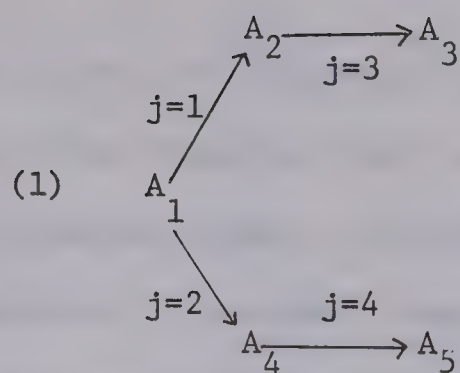
STEP 1 Reaction rates for each reaction step, r_{ij} , were determined from the principle of rate balance for each assumed chemical reaction model. The physical realizability of each model was checked by examining the values of reaction rate for each step in the reaction system.

STEP 2 Non-linear estimation was employed to obtain values for k_{ij} and n_{ij} . The physical realizability was again checked by the values of parameters thus obtained.

STEP 3 The variance (or goodness of fit) over the entire range of data encompassed was obtained for each kinetic model. The variance used may be defined as follow:

$$\sigma_{TOT}^2 = \left(\frac{\sum_{i=1}^m \sigma_i^2}{m} \right)^{1/2} \quad (4-9)$$

As an example of this approach, the shape of the time-composition simulated data of example 1 suggested the following alternative networks of reaction steps may be feasible ones:



It is assumed that chemical insights alone do not provide a basis for discriminating between these alternative models.

In step 1, the calculation of reaction rate values for each reaction step, it was observed that the values of $r_{11} = r_2 + r_{23}$ of model (1) are negative in sign. This suggests that the rate of disappearance of component, A_2 , is much faster than the rate of formation of A_2 from A_1 . This cannot be true if no amount of A_2 is initially present since component, A_2 , appears as an intermediate. Thus, model (1) can be eliminated from the subsequent analysis.

The results from non-linear estimation of k_{ij} and n_{ij} for the remaining three models are tabulated in Table 23.

Models (3) and (4) require negative values for the order of reaction in some steps and thus are not considered to be physically realizable from the kinetics point of view. Model (2) not only shows the lowest value of variance for the combined data but also involves reaction steps which are all physically realizable. Model (2) is thus the most adequate of the four models.

Since the values of reaction rate at various compositions for each reaction step of an assumed model can be estimated, one can generally infer some notions about the order of the kinetics to be expected. For example, if C_i and r_{ij} were linearly proportional, first order kinetics will probably be suggested by non-linear estimation. On the other hand, if C_i and r_{ij} were inversely proportional then a negative order of kinetics may be anticipated, as for reaction steps, r_{43} in model (3), and both r_{22} and r_{44} in model (4).

TABLE 23
Values of Parameters, k_{ij} and n_{ij} for different Chemical

Models and Variance of the fit

Chemical Model	k_{11}	n_{11}	k_{22}	n_{22}	k_{23}	n_{23}	k_{43}	n_{43}	k_{44}	n_{44}	Variance for the combined data
(2)	1.401 $s^2=0.469 \times 10^{-8}$	1.997	0.093 $s^2=0.699 \times 10^{-6}$	1.017 $s^2=0.87 \times 10^{-5}$	0.252	1.000			0.061 $s^2=0.251 \times 10^{-5}$	0.397	0.0017
(3)	1.401 $s^2=0.469 \times 10^{-8}$	1.997	0.357 $s^2=0.467 \times 10^{-5}$	1.02			0.003 $s^2=0.424 \times 10^{-4}$	-0.16*	0.061 $s^2=0.251 \times 10^{-5}$	0.397	0.003
(4)	1.401 $s^2=0.469 \times 10^{-8}$	1.997	0.015 $s^2=0.225 \times 10^{-5}$	-0.132* $s^2=0.438 \times 10^{-4}$	1.339	2.063			0.003 $s^2=0.424 \times 10^{-4}$	-0.162*	0.0094

* physically not realizable

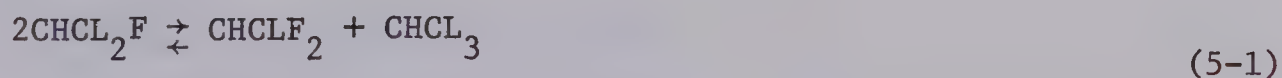
CHAPTER V

APPLICATION OF THE METHOD DEVELOPED FOR ANALYSIS OF MULTIPLE-STEP KINETIC DATA

To demonstrate the applicability of the method developed for decomposing multiple-step kinetic models into multiple single-step models (section 2.2.), two published reaction systems [7,9], (1) catalytic disproportionation of freons, and, (2) catalytic oxidation of naphthalene have been re-examined.

5.1. Example 2, Catalytic Disproportionation of Freons

Cavaterra, Fattore, and Giordano [7] have studied the catalytic disproportionation of CHCl_2F , pure chlorofluoromethane, on a highly fluorinated alumina catalyst at a reaction temperature of 200°C . Temperature variation along the reactor bed was kept within $\pm 2^\circ\text{C}$. Stoichiometrically, this reaction system can be described by the reversible reactions,



They assumed that the catalytic disproportionation could be represented by a sequence of intermediate steps involving interaction of each chemical species with catalyst; this interaction could be a halogen exchange reaction. From the experimental results and the nature of the system, they postulated the following pseudo-first-order kinetic model.

Using an abbreviated notation, the chemical model is,



Here, $A_1 = \text{CHCL}_2\text{F}$, $A_2 = \text{CHCLF}_2$, $A_3 = \text{CHF}_3$, $A_4 = \text{CHCL}_3$,
and U_0 , U_1 are fluorinating and chlorinating active centers of the catalyst, respectively.

The corresponding kinetic model which follows first-order kinetics is described by equations (5-3):

$$\begin{aligned}
 \frac{dC_1}{dt} &= -k'_{11}U_0C_1 - k'_{14}U_1C_1 + k'_{22}U_1C_2 \\
 \frac{dC_2}{dt} &= k'_{11}U_0C_1 - k'_{22}U_1C_2 - k'_{23}U_0C_2 \\
 \frac{dC_3}{dt} &= k'_{23}U_0C_2 \\
 \frac{dC_4}{dt} &= k'_{14}U_1C_1
 \end{aligned} \tag{5-3}$$

At the steady state, the concentrations of active centers, U_0 and U_1 , are constant and consequently, equation (5-3) reduces to,

$$\begin{aligned}
 \frac{dC_1}{dt} &= -k_{11}C_1 - k_{14}C_1 + k_{22}C_2 \\
 \frac{dC_2}{dt} &= k_{11}C_1 - k_{22}C_2 - k_{23}C_2
 \end{aligned}$$

$$\frac{dC_3}{dt} = k_{23}C_2 \quad (5-4)$$

$$\frac{dC_4}{dt} = k_{14}C_1$$

In brief, the reaction system can be described by the network of steps shown below,

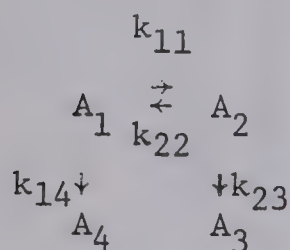


Figure 20

Applying the method of analyzing first order systems developed by Wei and Prater to the reaction system, they found that the results of this treatment were consistent with the experimental kinetic data. A chemical model involving halogen exchange intermediate reactions between reagents and catalyst was used to explain the reaction kinetics within experimental error.

5.2. Object of Present investigation

It is the aim of this second example to demonstrate again the applicability of the method described in section (2.2.2.1), namely that

(1) the reversible reaction step, in the absence of knowledge of the equilibrium constant, can be estimated by non-linear approximation;

(2) the order of reaction for each reaction step in such a complex reaction system may be estimated from the experimental data directly without any prior restrictive assumptions in the analysis.

TABLE 24
EXAMPLE 2
DISPROPORTIONATION REACTION OF PURE CHCL2F AT 200 DEG. C
CAVATERRA, FATTORE, AND GIORDANO EXPERIMENTAL DATA
JOURNAL OF CATALYSIS 8, 137-144 (1967)

TIME* (SEC.)	REACTION COMPONENT (MOLE FRACTION) CHCL2F	CHCLF2	CHF3	CHCL3
0.30000	0.85000	0.06300	0.00200	0.08500
0.50000	0.78000	0.10600	0.00400	0.11000
1.70000	0.43500	0.23900	0.03500	0.29100
2.00000	0.37800	0.25500	0.03600	0.33100
2.30000	0.31800	0.26800	0.04700	0.36700
2.70000	0.28900	0.27700	0.05500	0.37900
3.30000	0.22500	0.28600	0.07200	0.41700
3.70000	0.20100	0.28600	0.07800	0.43500
4.00000	0.17600	0.26200	0.07800	0.48400
6.70000	0.08600	0.21500	0.17200	0.52700
8.00000	0.05000	0.12000	0.23500	0.59500

* PRIVATE COMMUNICATION WITH THE AUTHORS

The experimental data were tabulated as shown in Table 24. The reaction times listed in the table were not published but were made available through the courtesy of the authors.

5.3. Application of the Method in Section (2.1.3.) to the Analysis

The procedure described in section (2.1.3.), when applied to the analysis of catalytic disproportionation of freons, may be summarized as shown in the following sections.

5.3.1. Smoothing of the Experimental Data

The smoothing functions fitted to the experimental data for each reacting component are listed in Table 25.

TABLE 25

Smoothing Function for Each Reacting Component

Reacting Component	Smoothing Function	Variance of the fit
CHCL_2F	$0.542e^{(-0.296T)} + 0.473e^{(-904T)}$	0.595×10^{-4}
CHCLF_2	$(1.389T) / [52.48 - 48.349e^{(-0.04T)} + 1.105e^{(0.505T)}]$	0.124×10^{-3}
CHF_3	$-0.045 \text{ARCTAN}(T)^{-0.36} + 0.057e^{0.196T} + 0.28e^{(-10T)}$	0.133×10^{-4}
CHCL_3	$1.164 / [1.492 + 4.126T^{-0.997}]$	0.198×10^{-3}

The data regenerated by the smoothing functions were checked by a material balance calculation of the total number of moles present at various times. Since the number of moles must remain constant for "unimolecular" stoichiometry, the material balances in Table 26 should

TABLE 26

EXAMPLE 2

DISPROPORTIONATION REACTION OF PURE CHCL₂F AT 200 DEG. C
EXPERIMENTAL COMPOSITION POINTS REGENERATED FROM FITTED FUNCTIONS

TIME (SEC.)	MOL FRACTIONS		REACTING COMPONENTS		TOTAL COMPONENT	
	CHCL ₂ F	CHCLF ₂	CHF ₃	CHCL ₃	BALANCE	
0.30000	0.85753	0.06930	0.00207	0.07659	1.00550	
0.50000	0.76920	0.10617	0.00376	0.11967	0.99882	
1.70000	0.42967	0.23580	0.03425	0.29683	0.99655	
2.00000	0.37760	0.25265	0.04012	0.32716	0.99754	
2.30000	0.33365	0.26534	0.04601	0.35390	0.99891	
2.70000	0.28502	0.27674	0.05408	0.38499	1.00085	
3.30000	0.22807	0.28396	0.06696	0.42394	1.00295	
3.70000	0.19800	0.28323	0.07624	0.44590	1.00338	
4.00000	0.17862	0.28017	0.08363	0.46066	1.00309	
6.70000	0.07567	0.19187	0.17232	0.55150	0.99137	
8.00000	0.05107	0.13749	0.23452	0.57901	1.00211	

always approach the value of unity for the assumed initial number of moles. It is obvious that the error is less than 1%. The units used for reacting component were mole fraction.

5.3.2. Reaction Rate

The reaction rate for each reacting component were obtained by differentiating the smoothing functions and were tabulated in Table 27. Except the first and last two points, the error in the rate balance is less than $\pm 1\%$. The experimental composition data of CHF_3 component, as shown in Table 24, have not only relatively low mole fraction values, but also widely scattered data points. Attempts to use less than five parameters to determine the smoothing function for CHF_3 data points were made but the smoothing function thus obtained deviated considerably at the beginning and end of the reaction period. The use of an empirical function with six parameters succeeded in correlating the data points reasonably well. This can be seen in Table 26 under the column with heading CHF_3 .

As discussed in chapter 2, when more than five parameters were used to characterize the smoothing function, the smoothing tended to approach the case of exact polynomials fitting, i.e. although the empirical function obtained with a large number of parameters tends to pass through most of the data points, only a small amount of smoothing has been done by the resulting function. The first value for the reaction rate of CHF_3 , at 0.3 second reaction time, was not found to be positive, as it should be from kinetic point-of-view, since it only appears as an intermediate component. This may be attributed to the use of the large number of

parameters just described. Because of the erroneous sign for the reaction rate value for CHF_3 at 0.3 sec reaction time, the rate balance is about -0.09 in error, as have shown in Table 27.

Using the present smoothing technique, the search for an empirical function with less than five parameters to smooth a set of limited and widely scattered ($\pm 10\%$ error, within 95% confidence level) data points, is very difficult to achieve. This situation improved considerably when reasonable numbers of data points were available, like in example 1 (19 points).

5.3.3. Estimation of Reversible Reaction Steps

As the reacting components A_1 and A_4 are the two major ones in the reaction system, better accuracy in data smoothing and reaction rate for these two may be expected. Because of this, the reaction steps r_{11} , r_{14} , and r_{22} around the reacting component A_1 were chosen to estimate rate constants and order of reactions for the forward and backward reversible steps, r_{11} and r_{22} . The differential rate equation for component A_1 , and which describe the kinetic model will be,

$$\frac{dC_1}{dt} = -k_{11}C_1^{n_{11}} - k_{14}C_1^{n_{14}} + k_{22}C_2^{n_{22}}$$

$$\text{i.e. } \frac{dC_1}{dt} + \frac{dC_4}{dt} = k_{22}C_2^{n_{22}} - k_{11}C_1^{n_{11}} \quad (5-5)$$

The values of $\frac{dC_1}{dt} + \frac{dC_4}{dt}$ calculated from Table 27 and the corresponding smooth values of C_2 and C_1 are listed in Table 28.

TABLE 27

EXAMPLE 2

DISPROPORTIONATION REACTION OF PURE CHCL ₂ F AT 200 DEG. C				
TIME (SEC.)	CHCL ₂ F	REACTION RATE CHCLF ₂	OF CHF ₃	TOTAL RATE BALANCE
0.30000	-0.47375	0.20084	-0.04490	-0.08816
0.50000	-0.41121	0.16898	0.03231	-0.00779
1.70000	-0.18918	0.06388	0.01977	0.00236
2.00000	-0.15904	0.04887	0.01953	0.00409
2.30000	-0.13480	0.03603	0.01981	0.00488
2.70000	-0.10948	0.02140	0.02063	0.00459
3.30000	-0.08211	0.00331	0.02247	0.00218
3.70000	-0.06878	-0.00678	0.02402	-0.00004
4.00000	-0.06063	-0.01347	0.02530	-0.00177
6.70000	-0.02308	-0.04275	0.04196	0.00017
8.00000	-0.01533	-0.03953	0.05400	0.01773

TABLE 28

Reaction Rate r_1+r_4 and Concentration of Component A_2 , A_1
in Example 2

Reaction time (sec)	$\frac{dC_1}{dt} + \frac{dC_4}{dt}$	A_2 (mole fraction)	A_1 (mole fraction)
0.3	-0.2441	0.0693	0.8575
0.5	-0.209	0.1061	0.7692
1.7	-0.0812	0.2358	0.4296
2.0	-0.0643	0.2526	0.3776
2.3	-0.0509	0.2653	0.3336
2.7	-0.0374	0.2767	0.285
3.3	-0.0236	0.2839	0.228
3.7	-0.0172	0.2832	0.198
4.0	-0.0135	0.2801	0.1786
6.7	-0.0009	0.1918	0.0756
8.0	-0.0032	0.1374	0.051

Using non-linear estimation with Rosenbrock's Hill-Climbing method, the values, $k_{22}=0.11648$, $n_{22}=1.029$, $k_{11}=0.2964$, and $n_{11}=1.164$ were calculated. The remaining two single reaction steps, r_{14} and r_{23} can be estimated by using the following two equations,

$$\frac{dC_3}{dt} = k_{23} C_2^{n_{23}}$$

$$\frac{dC_4}{dt} = k_{14} C_1^{n_{14}} \quad (5-6)$$

respectively. The values of $\frac{dC_3}{dt}$, $\frac{dC_4}{dt}$ were listed in Table 27, and the corresponding smoothed composition data, C_2 and C_1 , were in Table 26.

Table 29a gives a comparison of rate constant values obtained by this work with those from the relative rate constant matrix, reported by Cavaterra et al who employed the methods of kinetic structural analysis developed by Wei and Prater

TABLE 29a

Comparison of Parameters (relative) obtained by this work with
Cavaterra's Results

ij	Cavaterra et al (Wei-Prater approach)		This Work		
	Relative Rate Constant k''_{ij}	order of Reaction n_{ij}	Absolute Rate Constant k_{ij}	Relative Rate Constant k''_{ij}	order of Reaction n_{ij}
11	1	1	0.2974	1	1.168
14	0.89	1	0.2655	0.8927	1.028
22	0.547	1	0.1097	0.3689	1.024
23	0.429	1	0.0689	0.2316	0.742

The relative rate constants, k''_{ij} , obtained from this work and listed in Table 28, were obtained by dividing the absolute value of each rate constant k_{ij} by that of k_{11} . From Table 29a, a meaningful comparison of the

relative rate constants reported by Cavaterra with the ones obtained by this work cannot be made unless the non-linearity of the order of reaction obtained in the present work is taken into consideration.

A better comparison of the rate constants, taking order of reaction into consideration, can be achieved by plotting the reaction paths calculated from the kinetic model for both of the cases against the experimental data points. To do this, the relative rate constants k_{ij} obtained by Cavaterra, transformed to the absolute values by regarding the rate constant $k_{14}=0.2655$ for both of the cases. This is justified if we recognise that n_{14} of this work is approximately first order kinetics. Now, the balance of the rate constants can be determined by using relative ratio multiply by the absolute value of $k_{14}=0.2655$.

TABLE 29b

Comparison of Parameters (absolute) Obtained by This Work
with Cavaterra's Results

ij	Cavaterra et al (Wei-Prater approach)		This Work	
	Rate Constant k_{ij}	Order of Reaction n_{ij}	Rate Constant k_{ij}	Order of Reaction n_{ij}
11	0.2983	1	0.2974	1.168
14	0.2655	1	0.2655	1.028
22	0.1631	1	0.1097	1.024
23	0.1279	1	0.0689	0.742

Using the parameters tabulated in Table 29b and the following differential rate equations, to described the kinetic model,

$$\begin{aligned}\frac{dC_1}{dt} &= -k_{11}^{n_{11}} - k_{14}C_1^{n_{14}} + k_{22}C_2^{n_{22}} \\ \frac{dC_2}{dt} &= k_{11}C_1^{n_{11}} - k_{22}C_2^{n_{22}} - k_{23}C_2^{n_{23}} \\ \frac{dC_3}{dt} &= k_{23}C_2^{n_{23}} \\ \frac{dC_4}{dt} &= k_{14}C_1^{n_{14}}\end{aligned}\tag{5-7}$$

The reaction paths for both of the cases were calculated. They were plotted against the experimental data points in Figure 21.

5.3.4. Discussions

In Figure 21, the solid line is the reaction path calculated from the kinetic model with rate constants and order of reaction obtained by this work. The dashed line represents the composition data calculated for the same kinetic model but using the rate constants listed in Table 29 under the heading Cavaterra et al, (Wei-Prater approach).

The calculated reaction paths of both cases for components, CHCl_2F and CHCl_3 fit the experimental data equally well. As for CHF_3 and CHCl_3 components, the solid lines seem to pass through the characteristic trend of most of the data points but fail to predict the last ones, corresponding to reaction times of 8 secs. This is due to the fact that the smoothing technique and the non-linear estimation used in this work corresp-

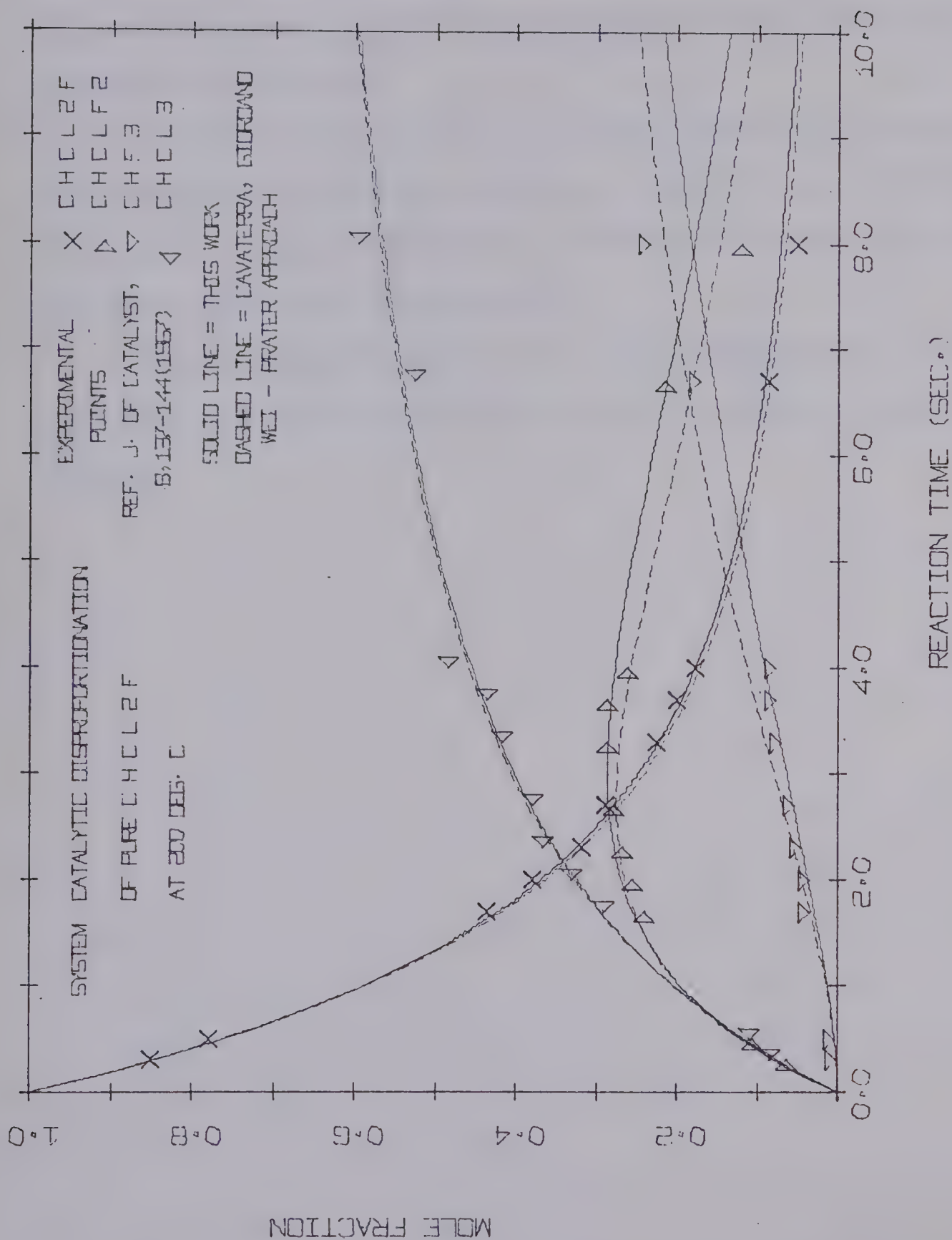


Figure 21 COMPARISON OF KINETIC MODELS

ond somewhat to equal weight for all data points. Here, although it is difficult to conclude which reaction path predicts the experimental data more satisfactorily, the following conclusions may be drawn for the method used in this work.

(1) Order of reaction for each reaction step can be estimated from the experimental data directly without any restrictive assumptions such as all reaction steps follow first order kinetics that Cavaterra and his co-workers have made in their analysis.

(2) The reversible reaction step can be approximated by non-linear estimation as described in section (2.2.2.1.) without the equilibrium constant.

5.4. Example 3, Catalytic Oxidation of Naphthalene

As described earlier in section (2.2.2.), the apparent reaction steps in this reaction system formed a closed loop. This example demonstrates the applicability of the method described in section (2.2.2.). In view of the importance of the catalytic oxidation of naphthalene reaction in the manufacture of phthalic anhydride, further study is of interest. The data of D'Alessandro and Farkas [9] were employed in this example. It is also worth noting that this is a multiple-step heterogeneous catalytic reaction system. Irrespective of diffusional problems which may exist the modeling procedure is analogous to that employed for homogeneous reaction systems.

D'Alessandro and Farkas studied the vapor phase catalytic oxidation of naphthalene over a catalyst of vanadium pentoxide. The reaction was carried out in the presence of a large excess of oxygen under conditions such that a negligible change in volume was encountered over a temperature range from 340°C to 475°C .

In their mechanistic analysis, they first grouped the highly oxidized and relatively low conversion products like maleic anhydride, carbon monoxide, and carbon dioxide. They proposed the reaction scheme of Figure 22 with the restrictive assumption that all reaction steps follow first order kinetics. Using the D'Alessandro's abbreviation for the reacting components the chemical model is as shown in Figure 22.

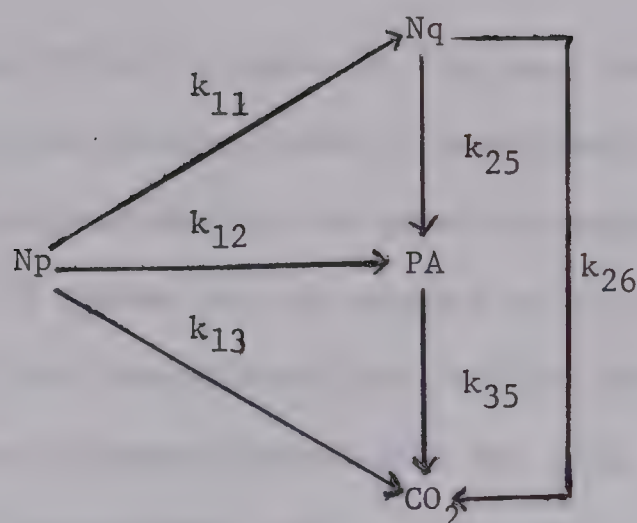


Figure 22.

The differential rate equations for this system will be,

$$\frac{dC_{Np}}{dt} = -(k_{11} + k_{12} + k_{13}) C_{Np}$$

$$\frac{dC_{Nq}}{dt} = k_{11}C_{Np} - (k_{24} + k_{26}) C_{Nq}$$

(5-8)

$$\frac{dC_{PA}}{dt} = k_{24}C_{Nq} + k_{12}C_{Np} + k_{35}C_{PA}$$

$$\frac{dC_{CO_2}}{dt} = k_{13}C_{Np} + k_{26}C_{Nq} + k_{35}C_{PA}$$

Because the solution to the above system of differential equations cannot be obtained explicitly, they suggested obtaining the relative rate constants of PA, Nq, CO₂ first by extrapolation of the product distribution to zero conversion. Since these are assumed to be first order plots, the relative values of the initial rates are proportional to the intercepts thus obtained. If it is assumed that the rate constants are also proportional to the initial rates (which is a mathematical consequence of the assumed linear kinetics), then one obtains the ratios,

$$k_{11} : k_{12} : k_{13} = 0.4 : 0.4 : 0.2$$

The remaining relative values of the rate constants, k_{24} , k_{26} , and k_{35} are adjusted to the proposed model by trial-and-error. The data used in their analysis was measured at the reaction temperature of 410°C . Two different sets of values for the unknown rate constants were reported, and a comparison of the composition distribution curves plotted from these models, with that of the experimental ones was made. They found neither model satisfied the experimental data. As a remedy, they argue that since the concentration of carbon monoxide plus carbon dioxide does not increase with conversion, whereas the concentration of maleic anhydride does increase with conversion, a better reaction scheme will be given by

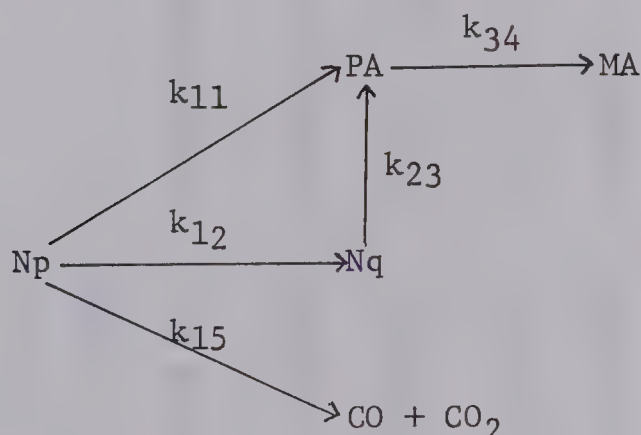


Figure 23

In this thesis, the latter chemical model is called model 2.

5.4.1. Smoothing and Differentiation of the Experimental Data

Because of the limited amount of data available at reaction temperatures other than 410°C , and the scattering apparent in the limited data, in this work, only the data at 410°C were examined. The isothermal experimental data employed are shown in Table 30.

An illustration of how the criterion of a material balance check can

TABLE 30

EXAMPLE 3 INPUT DATA *

CATALYTIC OXIDATION OF NAPHTHALENE, NOMINAL TEMP: 410 DEG. C, EXPT. NO. 3

RESIDENCE TIME (SEC.)	NP/NPO	PA/NPO	MA/NPO	NQ/NPO	CO ₂ /NPO	CO/NPO
0.044	0.7540	0.1520	0.0000	0.0674	0.0195	0.0068
0.065	0.5800	0.3180	0.0203	0.0441	0.0272	0.0108
0.086	0.5100	0.3590	0.0337	0.0551	0.0328	0.0094
0.130	0.4000	0.4550	0.0288	0.0500	0.0469	0.0177
0.172	0.3130	0.5270	0.0356	0.0412	0.0662	0.0193
0.217	0.1770	0.6660	0.0496	0.0309	0.0465	0.0296

* JOURNAL OF COLLOID SCIENCE, VOL. 11, P.658, 1956

TABLE 31
EXAMPLE 3
COMPOSITION DATA REGENERATED FROM THE FITTED FUNCTIONS

RESIDENCE TIME (SFC.)	NP/NPO	PA/NPO*	MA/NPO	NQ/NPO	CO2/NPO	CO/NPO	MATERIAL BALANCE
0.044	0.7207	0.2064	0.0218	0.0674	0.0254	0.0060	1.0476
0.065	0.6165	0.2745	0.0216	0.0618	0.0307	0.0086	1.0137
0.086	0.5276	0.3366	0.0225	0.0567	0.0352	0.0112	0.9898
0.130	0.3817	0.4544	0.0278	0.0473	0.0433	0.0168	0.9713
0.171	0.2830	0.5537	0.0362	0.0400	0.0498	0.0220	0.9846
0.217	0.2029	0.6563	0.0492	0.0331	0.0563	0.0280	1.0258

* FUNCTION FITTED FOR COMPONENT PA/NPO = $2.0302 * \text{TANH}(T) ** 0.73$

TABLE 32
EXAMPLE 3

COMPOSITION DATA REGENERATED FROM THE FITTED FUNCTIONS

RESIDENCE TIME (SEC.)	NP/NPO	PA/NPO*	MA/NPO	NQ/NPO	CO2/NPO	CO/NPO	MATERIAL BALANCE
0.044	0.7207	0.1899	0.0218	0.0674	0.0254	0.0060	1.0312
0.065	0.6165	0.2668	0.0216	0.0618	0.0307	0.0086	1.0060
0.086	0.5276	0.3421	0.0225	0.0567	0.0352	0.0112	0.9953
0.130	0.3817	0.4746	0.0278	0.0473	0.0433	0.0168	0.9915
0.171	0.2830	0.5662	0.0362	0.0400	0.0498	0.0220	0.9971
0.217	0.2029	0.6374	0.0492	0.0331	0.0563	0.0280	1.0069

* FUNCTION FITTED FOR COMPONENT, PA/NPO = 0.756*TANH(5.67*T)

help one to choose the "smoothing fitting" from two different fitted functions, whose variances are about the same, will be presented. Table 31 shows a material balance which was checked by regenerating the composition data from the two fitted functions. The phthalic anhydride reacting component was used for the material balance and the smoothing functions employed were

(a) $2.0302 \text{TANH}(T)^{0.73}$ and

(b) $0.7563 \text{TANH}(5.67T)$

From Table 32, it is obvious that the better material balance for the whole reaction system was obtained fitting the second of the two functions. Though their error variances are approximately equal, the former being 0.123×10^{-2} and the latter 0.134×10^{-2} , the second function was chosen because of its better material balance.

In calculating the compositions of Table 32, the functions used to fix the data for the balance of the reacting components are shown in Table 33.

Table 33

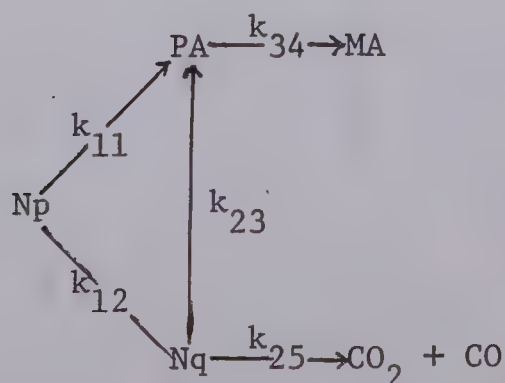
Smoothing Functions for Each Reacting Component (Example 3)

Component	Function Fitted	
Np	$0.588e^{(-8.55T)} + 0.414e^{(-6.06T)}$	0.155×10^{-2}
CO	$0.13T + 10^{(-1.72T)} - 0.999e^{(-3.9T)}$	0.67×10^{-5}
CO ₂	$0.017T^{0.239} + 0.109T^{0.59}$	0.143×10^{-3}
MA	$0.58T + 10^{(-1.09T)} - 0.97e^{(-1.8T)}$	0.166×10^{-5}
Nq	$0.08e^{(-4.1T)} - 0.08e^{(0.99 \times 10^8 T)}$	0.801×10^{-5}

The reaction time, T , was used as the independent variable in the fitted function. Because of the wide scattering of the experimental data points (especially for the low concentration values for reacting components like maleic anhydride and carbon monoxide, and the limited number of time-composition data points available, the material balance is not very satisfactory for the first point in Table 31. The wide scattering of the data may be due to a 7°C range in catalyst temperature during the experiments.

Table 34 shows the first derivatives obtained by differentiating the fitted functions corresponding to each of the six reacting components. The sum of reaction rates for all components at a common instantaneous time must equal zero. This "rate balance" shown in the extreme right column is not very satisfactory, especially the first point. The same reasons for the inconsistent material balance just mentioned are applicable and the error originated from the fitted functions is magnified considerably by taking the first derivatives.

At this stage of the calculations, all of the reaction rate values for the reacting components and the corresponding smoothed composition data are known. In addition to the kinetic model 2, model 1, proposed by Ioffe et al [18] during their study of the same reaction system as described earlier in section (1.1.2.) is shown below



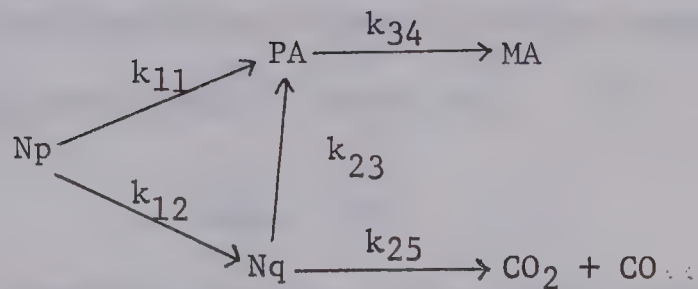
Model 1

TABLE 34
EXAMPLE 3

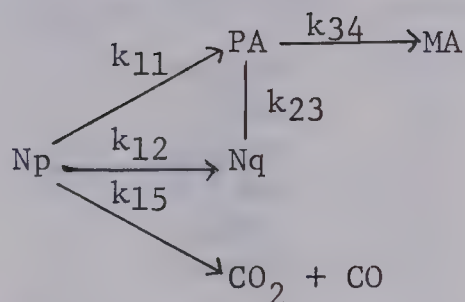
REACTION RATE OBTAINED BY DIRECT DIFFERENTIATION OF THE FITTED FUNCTIONS						
RESIDENCE TIME (SEC.)	RNP	RPA	RMA	RNQ	RCO2	RCO REACTION RATE BALANCE
0.044	-5.3755	4.0329	0.0000	-0.2769	0.4481	0.1209 -1.0504
0.065	-4.5779	3.7555	0.0183	-0.2539	0.3642	0.1227 -0.5710
0.086	-3.9012	3.4116	0.0697	-0.2330	0.2916	0.1242 -0.2370
0.130	-2.7961	2.6006	0.1661	-0.1945	0.1702	0.1268 0.0731
0.171	-2.0554	1.8854	0.2440	-0.1643	0.0875	0.1287 0.1259
0.217	-1.4597	1.2428	0.3187	-0.1360	0.0212	0.1303 0.1174

5.4.2. Selection of the Best-Fitting Chemical Model

Chemical model 1



Chemical model 2



Applying the procedure for the loop reaction system described in section (2.2.2.), reaction steps r_{11} and r_{23} were estimated by non-linear estimation.

From the principle of rate balance, both models give

$$r_{PA} = r_{11} + r_{23} - r_{MA},$$

$$\text{or } r_{PA} + r_{MA} = k_{11}(C_{Np})^{n_{11}} + k_{23}(C_{Nq})^{n_{23}} \quad (5-9)$$

The reasons for choosing reaction steps r_{11} and r_{23} around PA reacting component are as follows:

- (1) PA is a major component in the reaction system and, as a result, the first derivative can be obtained more accurately than for the rest of the components;
- (2) the reaction steps, r_{11} and r_{23} , are equivalent in both the models, i.e. the values of k_{11} , n_{11} , k_{23} and n_{23} obtained from

non-linear estimation apply to both models.

From Table 34 the left-hand-side of equation (5-9), $-r_{PA} + r_{MA}$, can be calculated. The rate data thus obtained and the corresponding concentrations of C_{Np} and C_{Nq} are listed in Table 35.

Table 35

Values of reaction rate ($r_{PA} + r_{MA}$) and concentration C_{Np} , C_{Nq}

Reaction time (sec.)	$r_{PA} + r_{MA}$	C_{Np}	C_{Nq}
0.044	4.0329	0.7207	0.0674
0.065	3.7739	0.6165	0.0618
0.086	3.4813	0.5276	0.0567
0.13	2.7668	0.3817	0.0473
0.171	2.1294	0.283	0.0400
0.217	1.5615	0.2029	0.0331

In equation (5-9), k_{11} , n_{11} , k_{23} and n_{23} are unknown parameters which may be estimated by fitting the function, $k_{11}(C_{Np})^{n_{11}} + k_{23}(C_{Nq})^{n_{23}}$ to the rate data and by using Rosenbrock's Hill-climbing Method to minimize the residual sum of the squares between the observed rate values and that of the calculated ones. The parameters were found to be optimal when $k_{11} = 5.137$, $n_{11} = 0.7154$, $k_{23} = 1.2298$, and $n_{23} = 0.8935$, with a variance of 0.0354.

For Kinetic model 1, since the rates for the reaction step, r_{11} can be calculated from, $r_{11} = k_{11}(C_{Np})^{n_{11}}$, thus $r_{12} = -r_{Np} - r_{11}$ can also be calculated. The rate values for reaction steps, r_{12} , r_{25} , and r_{34} are recorded in Table 36.

Table 36

Values of rate for reaction step, r_{12} , r_{23} , and r_{34}

Reaction time (sec.)	r_{12}	$r_{34} = r_{MA}$	$r_{25} = r_{CO_2} + CO$
0.044	1.3112	0.0	0.5691
0.065	0.9436	0.0183	0.487
0.086	0.6498	0.0697	0.4158
0.13	0.217	0.1661	0.2971
0.171	-0.2695	0.244	0.2163
0.217	-0.1818	0.3187	0.1516

In the same manner, the reaction step, r_{12} , in Kinetic model 2 can be calculated from $r_{12} = -r_{Np} - r_{11} - r_{15}$.

Table 37

Values of rate for reaction steps, r_{12} , r_{34} , and r_{15}

Reaction time (sec.)	r_{12}	$r_{34} = r_{MA}$	$r_{15} = r_{CO_2} + CO$
0.044	0.742	0.0	0.5691
0.065	0.4566	0.0183	0.487
0.086	0.2339	0.0697	0.4158
0.13	-0.8013	0.1661	0.2971
0.171	-0.2432	0.244	0.2163
0.217	-0.3335	0.3187	0.1516

Reaction step r_{34} in both of the models is a reaction between the intermediate PA and the final product MA, and so the estimated k_{34} and n_{34} values are good for both reaction schemes.

Routine application of the procedure of non-linear estimation for each reaction step yields the results tabulated in Table 37.

The kinetic models for the two chemical schemes are given by equa-

TABLE 38

Values of Parameters for Models (1) and (2),

Example 3

Kinetic Model	k_{11}	n_{11}	k_{23}	n_{23}	k_{34}	n_{34}	k_{12}	n_{12}	k_{25}	n_{25}	k_{15}	n_{15}	Variance for the combined data
(1)	5.137	0.715	1.229	0.893	0.991	2.485	3.456	2.827	82.07	1.843			0.01209
	$s^2=0.0354$		$s^2=0.0354$		$s^2=0.167 \times 10^{-3}$		$s^2=0.0195$		$s^2=0.254 \times 10^{-5}$				
(2)	5.137	0.715	1.229	0.893	0.991	2.485	3.426	4.530			0.799	1.033	0.02427
	$s^2=0.0354$		$s^2=0.0354$		$s^2=0.167 \times 10^{-3}$		$s^2=0.0504$				$s^2=0.457 \times 10^{-5}$		

tions (5-10) and (5-11). For model 1,

$$\begin{aligned}
 \frac{dC_{Np}}{dt} &= -k_{11}C_{Np}^{n_{11}} - k_{12}C_{Np}^{n_{12}} \\
 \frac{dC_{PA}}{dt} &= k_{11}C_{Np}^{n_{11}} + k_{23}C_{Nq}^{n_{23}} - k_{34}C_{PA}^{n_{34}} \\
 \frac{dC_{Nq}}{dt} &= k_{12}C_{Np}^{n_{12}} - k_{23}C_{Nq}^{n_{23}} - k_{25}C_{Nq}^{n_{25}} \\
 \frac{dC_{MA}}{dt} &= k_{34}C_{PA}^{n_{34}} \\
 \frac{dC_{CO_2 + CO}}{dt} &= k_{25}C_{Nq}^{n_{25}}
 \end{aligned}
 \tag{5-10}$$

and for model 2

$$\begin{aligned}
 \frac{dC_{Np}}{dt} &= -k_{11}C_{Np}^{n_{11}} - k_{12}C_{Np}^{n_{12}} - k_{15}C_{Np}^{n_{15}} \\
 \frac{dC_{PA}}{dt} &= k_{11}C_{Np}^{n_{11}} + k_{23}C_{Nq}^{n_{23}} - k_{34}C_{PA}^{n_{34}} \\
 \frac{dC_{Nq}}{dt} &= k_{12}C_{Np}^{n_{12}} - k_{23}C_{Nq}^{n_{23}} \\
 \frac{dC_{MA}}{dt} &= k_{34}C_{PA}^{n_{34}} \\
 \frac{dC_{CO_2 + CO}}{dt} &= k_{15}C_{Np}^{n_{15}}
 \end{aligned}
 \tag{5-11}$$

Integration of these kinetic models was possible by using the parameter values listed in Table 38 and a fourth order Runge-Kutta method.

The reaction paths calculated from the Kinetic models were

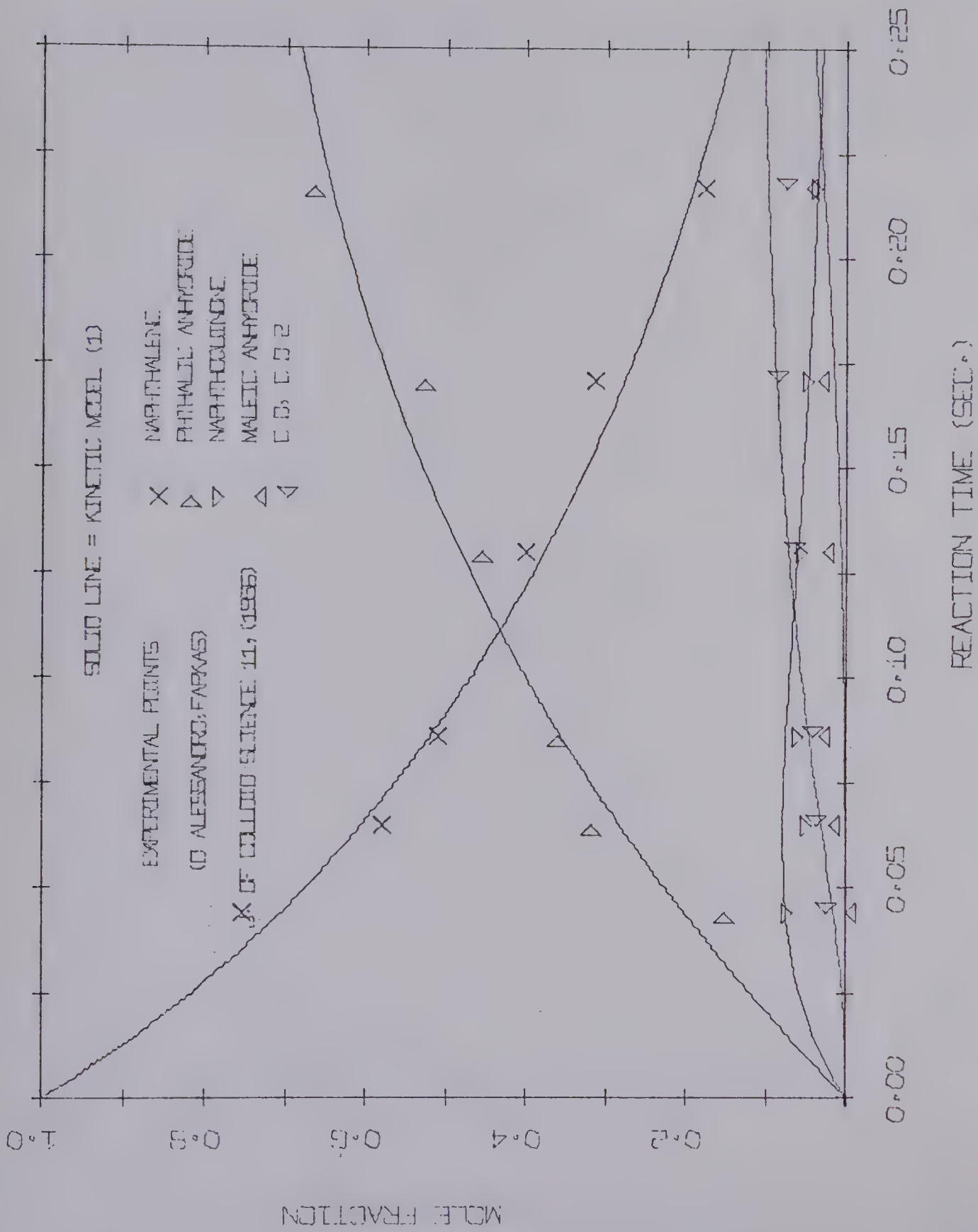


Figure 24 COMPARISON OF EXPERIMENTAL COMPOSITION WITH THE KINETIC MODEL
REACTION SYSTEM OXIDATION OF NAPHTHALENE AT 410 DEG. C, EXAMPLE NO. 3

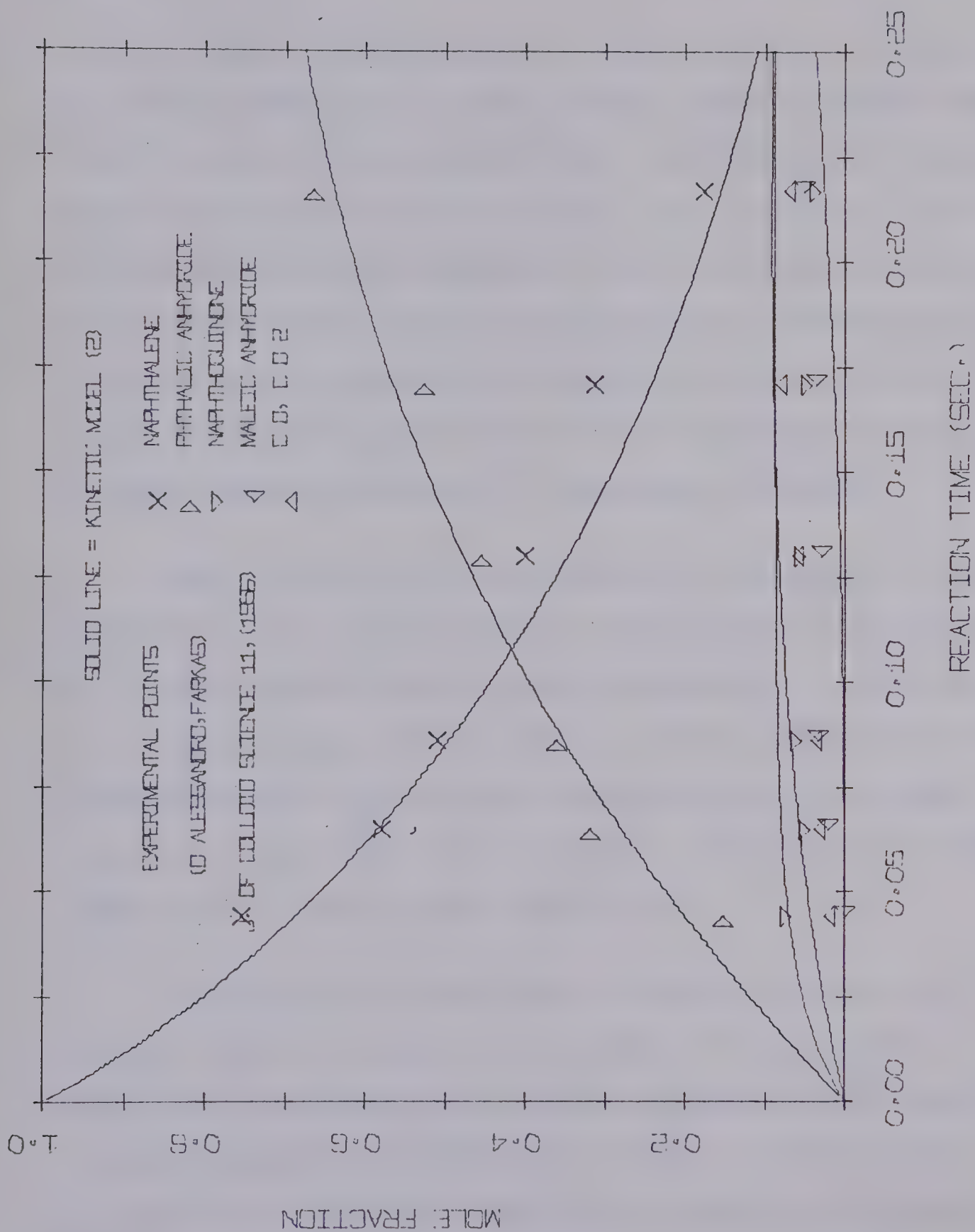


Figure 25 COMPARISON OF EXPERIMENTAL COMPOSITION WITH THE KINETIC MODEL
REACTION SYSTEM OXIDATION OF NAPHTHALENE AT 410 DEG. C, EXAMPLE NO. 3

compared with the experimental data. They are as shown in figures 24 and 25.

In figure 24, the calculated reaction paths are in good agreement with the experimental data, except for that of maleic anhydride which is slightly lower than the experimental one. On the whole, the accuracy is within the scattering of the experimental data. In figure 25, the calculated path of PA is in good agreement but the rest of the reacting components deviate significantly from the experimental data. From the results of the calculated reaction paths and the variances for the combined data, it appears that Kinetic model 1 fits the given experimental data more satisfactorily than model 2 proposed by D'Alessandro and Farkas.

Using the data of Ioffe and Sherman [18], Peterson [29] has investigated the same vapor phase oxidation of Naphthalene by non-linear estimation for the data between 260-400°C reaction temperature. The approach he used, of the type in category (2) in chapter 1, involves the numerical integrations of the differential equations and subsequently applying non-linear least squares to fit the data. From his analysis, he found that both Kinetic models 1 and 2, fitted the data equally well.

In Table 38, the values shown for orders of reaction, $n_{34} = 2.485$ and $n_{12} = 2.8279$, are physically meaningless. This is perhaps to be expected since the kinetic models are not comparable in form to mechanistic models such as Langmuir-Hinshelwood models. In addition, the use of six data points considerably restricts the validity of inferences which may be drawn. Nonetheless, the use of combined single-step power-law rate equations in modelling of complex reaction systems introduces an

element of compatibility between chemical and kinetic models. This aspect is missing when a complete model is assumed, and not constructed from the individual steps.

CHAPTER VI

DISCUSSION

6.1. Summary of the Method

The method proposed in this thesis for the interpretation of experimental isothermal kinetic data for multiple-step chemical reaction systems can be summarized as follows:

STEP I. Smoothing and Differentiation of the Experimental Data

A linear or non-linear function of similar shape is fitted . The parameters of the fitted function are estimated by minimizing the residual sum of the squares of differences between calculated and observed compositions using Rosenbrock's Hill-Climbing Method. Differentiation of the resulting functions provides local values of the reaction rates for each reacting component.

STEP II. Development of Alternative Chemical Reaction Step Models

If the overall chemical steps for the reaction system being calculated are unknown, networks of apparently feasible reaction steps must be devised. Such alternative chemical models are based upon the sequential and parallel chemical steps deduced from the concentration-time plots and/or additional chemical insights.

STEP III. Decomposition of Overall Rate Data Into Single Step Rate Data

Decompose the overall rate data for each reacting species into rate data for individual reaction steps using the rate balance method. A non-linear approximation for the estimation of two reaction steps is required when the coefficient matrix of the reaction

system is singular.

STEP IV. Evaluation of Kinetic Parameters for each Reacting Step in the Kinetic Model

The parameters, k_{ij} and n_{ij} , of the power function rate equation for each reaction step are estimated by minimizing the residual sum of squares as for step I.

STEP V. Discriminating between Chemical Models

Alternative chemical reaction-step models are checked by a sequential approach which relies on two criteria

- (1) physical realizability, and
- (2) statistical justification

6.2. Comments on Applicability of this Modelling Method

The procedure of Step I is obviously restricted to suitable time-composition data such as that measured with batch or integral reactors. However, at this stage of development, the application of the method to homogeneous system or to catalytic heterogeneous systems is identical in procedure. If differential rate data are available directly from the experiments, they may require smoothing but not differentiation. The method is not recommended for use when limited experimental data are available because of the resultant uncertainties inherent in curve-fitting methods. Five or six data points were considered to be minimal for modelling depending upon the complexity of the chemical models involved. The relevance of the kinetic model to the true chemical model is questionable when the time-concentration profiles for various components are clearly ambiguous, i.e. when the scatter in the data necessitates approximating of unknown functional forms.

When the requirements of sufficient kinetic data and clearly defined concentration-time trajectories are met, this approach to kinetic modelling should prove to be superior to other methods of analyzing non-linear models which model the complete kinetics simultaneously. This assertion is made on the basis that the method discriminates between the non-linearities of individual steps in the chemical model before constructing the overall kinetic model. With prior integral methods of analysis, only trial-and-error can be used in constructing suitable models. With complex systems, mathematical approximations rather than chemically relevant kinetics models result.

6.3. Conclusions

1. The first derivatives obtained by differentiating the smoothing functions used in this thesis give accurate results and their applicability to the interpretation of rate data for a multiple-step reaction system appears justified.

2. The order of reaction and rate constant for each reaction step can be evaluated from the isothermal experimental data without the conventional trial-and-error modelling procedure often used in other non-linear estimation methods.

3. The use of both integral and smoothed differential rate data provides an improved basis for discriminating between alternative chemical models prior to development of the kinetic model.

4. Situations involving reversible or closed (loop) reaction steps in a multiple-step chemical reaction system pose computational difficulties

in this method. This has been successfully resolved by use of non-linear approximations for these steps before decomposition of the network of steps.

5. The iterative computational procedure involved is very simple. The use of a direct search optimization procedure in evaluating parameters for each step should pose no problems since only two to five parameters are generally required per step.

6.4. Recommendations

1. The analysis of error variance of experimental data a priori to the application of the method is desirable. The correlation between the error variance of the experimental data with the accuracy of the parameters estimated by the method should be examined in more detail.

2. Sets of time-composition data with different initial values are recommended to obtain more accurate and consistent values of the parameters. This may be particularly effective in determining the value of the order of reaction for each component.

3. Use of spline function to smooth a limited experimental data available is worth considering.

NOMENCLATURE

\bar{a}	denote a column matrix (a_1, a_2, \dots, a_p)
b	parameter of the approximation to the rate equations, dimensionless
\bar{B}	the vector of the unknown coefficients, β_j , defined in equation (3.8)
C_A	concentration of reacting component A at time = t
C_{Ao}	initial concentration of A when time = 0
C_i	concentration of i^{th} component
e	error constant factor
e_i	the error which is assumed to be randomly distributed, i.e. with mean $\mu = 0$, variance s^2
E	normally distributed error around the true value, μ
f_{ij}	concentration dependent functional relationship terms of the rate equation, defined in equation (1-9)
F	molal feed rate, lb-moles feed/hr. in equation (3-14)
h	interval for equal spacing
k	reaction rate constant
K_i	dimensionless rate constant for the i^{th} reaction
k_i'	reaction rate constant in equation (5-3)
k_j	rate constant in equation (1-11)
m	the degree of polynomial, defined in equation (3-4)
m	the number of reacting componets in the reaction system in equation (4-9)
\bar{M}	coefficient matrix of the reaction step
n_{ij}	order of reaction for i^{th} component in j^{th} reaction
N	number of values of x_i to be used
N	number of data points in equation (3-17)
P	number of parameter in the fitted function in equation (3-17)

- $p_j(X_i)$ some as yet unspecified function of independent variable x and is of degree j
- Q the number of time intervals between the time at which the concentrations were measured
- r_i reaction rate for i^{th} component
 $= \sum_{j=1}^n r_{ij}$
- r_{ij} reaction rate for i^{th} component takes part in j^{th} reaction
 $= f(t, c_1, c_2, c_3, \dots), (i = 1, 2, \dots, m), (j = 1, 2, \dots, n)$
- \bar{r}_i column matrix of reaction rate for i^{th} component (r_1, r_2, \dots, r_m)
- \bar{r}_{ij} column matrix of reaction step r_{ij}
- s standard deviation in equation(4.5)
- t reaction time
- T independent variable, reaction time
 $= t$
- t' the time required to reach y_o for an arbitrary initial value of β
- t'_r the time required to reach a given value of $y_o (= \frac{C_A}{C_{Ao}})$ when $\beta_o = 1$
- u the index in equation (1-11) ($u = 1, 2, \dots, Q$)
- v_o fluorinating active centers of the catalyst
- v_1 chlorinating active centers of the catalyst
- W mass of catalyst, lb
- x conversion
 $= C_{Ao} - C_A$
- x_i a uniformly distributed random number
- \bar{X} denote a vector of column matrix (X_1, X_2, \dots, X_p)
- Y represents the resultant simulated data

y_o	dimensionless
	$= C_A / C_{Ao}$
Y_{iu}	$C_i(t_u) - C_i(t_o)$
ΔY_{iu}	experimental concentration values of reacting component
α_j	the j^{th} polynomial coefficient, defined in equation (3-4)
β_j	the coefficients of the power series
β_r	$\frac{C_B}{C_{Ao}}$, dimensionless, subscript r denotes a reference run for which $\beta_o = 1$
γ_j	the coefficients of the orthogonal polynomial in equation (3-11)
σ_{TOT}^2	variance for the complete set of data
σ_i^2	the variance of the fit for i^{th} component
μ	mean value
Δ	determinant multiresponse error criterion
Φ	integration constant in equation (1-26)

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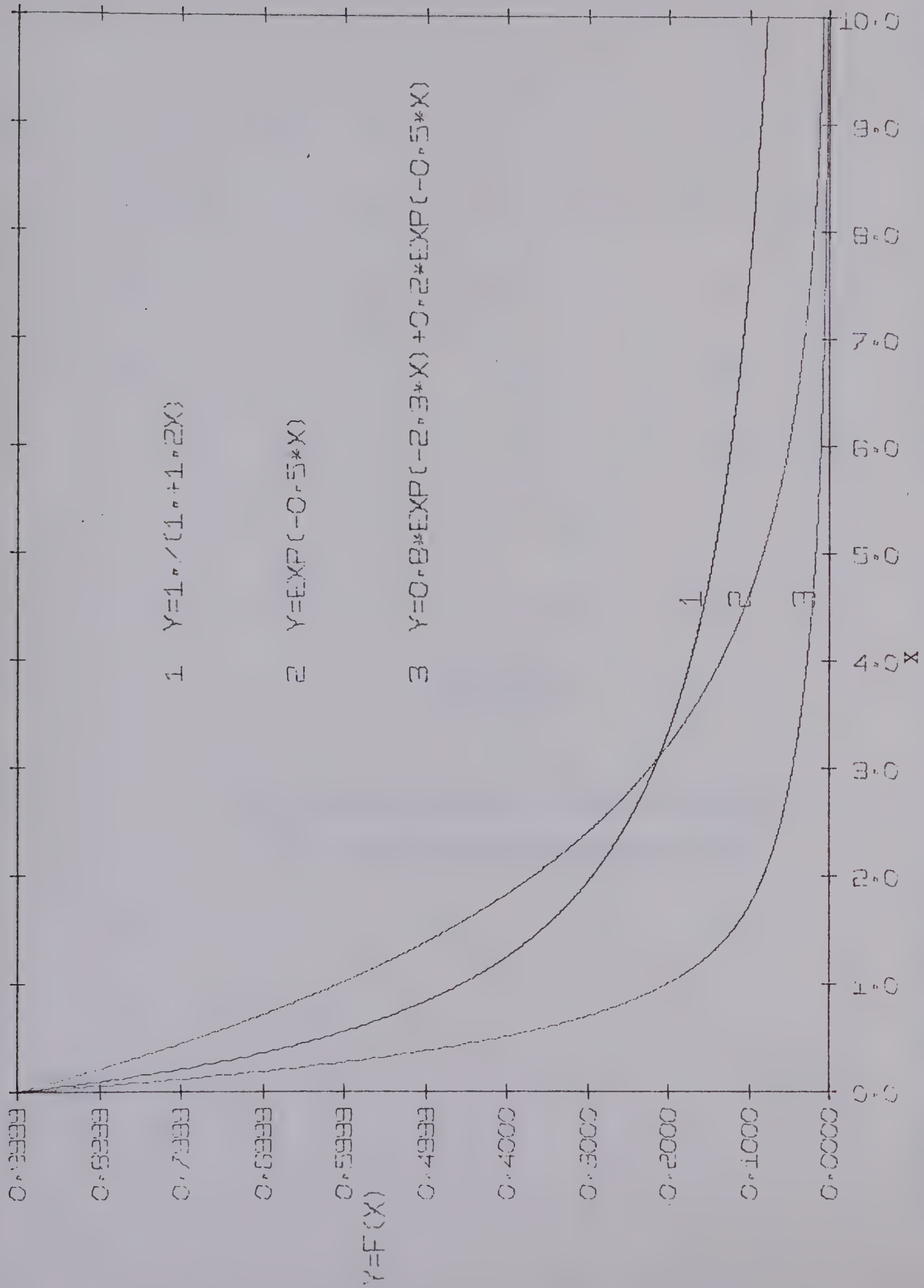
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APPENDIX 1

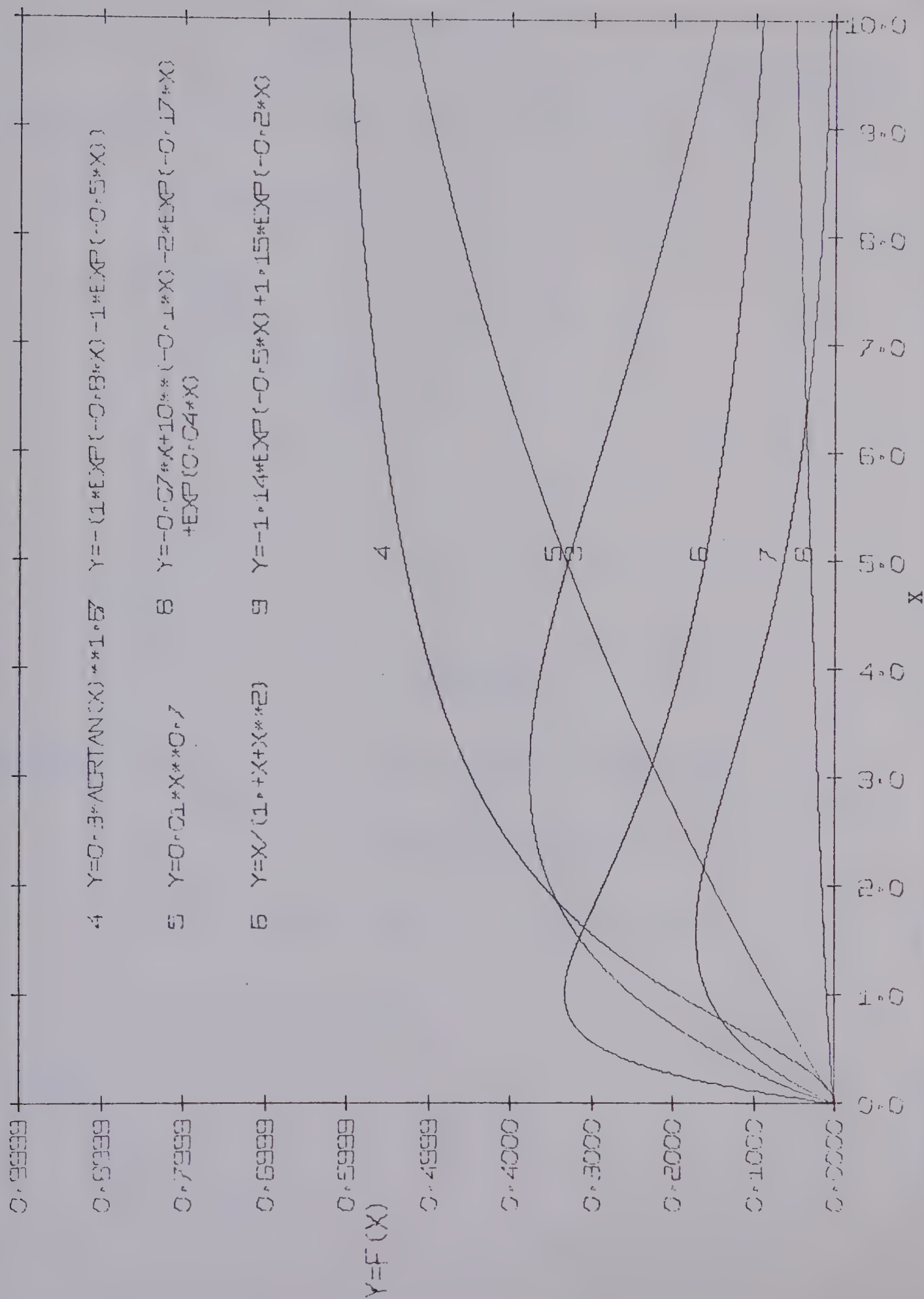
SOME COMMON FUNCTIONS THAT TAKE THE FORMS
OF THE REACTANT DISTRIBUTION KINETIC DATA



Appendix 1 Some common functions that take the forms of the reactant distribution kinetic data

APPENDIX 2

SOME COMMON FUNCTIONS THAT TAKE THE FORMS
OF THE PRODUCT DISTRIBUTION KINETIC DATA



Appendix 2 Some common functions that take the forms of the product distribution kinetic data

APPENDIX 3

DESCRIPTION OF INPUT AND READ IN. FORMAT FOR

ROSENBROCK'S METHOD

Appendix 3

Rosenbrock's Method

Description of Input Data and the read in Format for Rosenbrock's Hill-Climbing Method.

M = number of variables

N = number of data points

NFIT = number of fits

p = number of parameters

KPN = 0 if normalization desired

= 1 if not

M1 = maximum number of rotation (=50*P)

M2 = maximum number of steps between rotation (=75*P)

FORMAT (6I5) ()

XNAM(I,J) = title for the independent variable (Time)

DES(J) = description of the input function

FORMAT (20A3)

Y(I) = dependent variable (concentration for the present case)

FORMAT (F13.7)

X(I, 1) = independent variable (Reaction time)

ss = a constant

PAR1(2) = Parameter (I = 1,p)

FORMAT (6F12.7)

APPENDIX 4

COMPUTER PROGRAMS

C ROSEN METHOD

C ROSEN METHOD

```

C *****
C *
C * ROSENBROCK'S HILL-CLIMBING METHOD *
C *
C *****

```

```

      INTEGER P
      DIMENSION ELAM(9),DES(81),XNAM(9,9),KS(9),OV(9,9),X(40
*,1),Y(40),PA
      1R1(9),PAR3(9),KSF(9),KF(9)

```

```

C      THIS IS THE MAINLINE PROGRAM FOR ROSENBROCK'S METHOD
C
C      INPUT DATA READIN
C

```

```

      MXMN=0
      READ (5,1) M,N
      READ(5,2)((XNAM(I,J),J=1,5),I=1,M)
      READ (5,1) NFITS
      DO 3 I=1,N
      READ (5,5) X(I,1)
3  CONTINUE
      DO 4 I=1,N
      READ (5,5) Y(I)
4  CONTINUE
      5  FORMAT (F13.7)
      DO 6 NFT=1,NFITS
      READ (5,1) P,KPN,M1,M2
      1  FORMAT(6I5)
      READ(5,2) (DES(J),J=1,24)
      2  FORMAT (24A3)
      KP=P+1
      READ (5,7) SS,(PAR1(I),I=1,P)
      7  FORMAT (9F8.4)
      WRITE (6,8)
      8  FORMAT('1',/////////,48X,'A3 COMPONENT',/,48X,'-- -----
*---')
      WRITE(6,9)(DES(J),J=1,24)
      9  FORMAT ('0',35X,24A3,/)
      WRITE (6,10)
10  FORMAT (' ',32X,'PARAMETER ESTIMATES BY ROSENBROCK
* METHOD',/)

```

```

C      GENERATE INITIAL SET OF ORTHOGONAL VECTORS & NULL
C      SCALING FACTORS
C

```


C ROSEN METHOD ... (CONT'D)

```

DO 11 I=1,P
KSF(I)=0
11 PAR3(I)=PAR1(I)
34 DO 12 I=1,P
DO 13 J=1,P
13 OV(I,J)=0.0
12 OV(I,I)=1.0

```

C ADJUSTMENT OF PARAMETERS

C

```

CALL VARIA (PAR1,KSF,P,VAR2,N,NFT,X,Y)
VAR1=VAR2*(-1.0)**MXMN
VAR3=VAR1
COUNT=0.
DO 14 KKK=1,M1
DO 15 I=1,P
ELAM(I)=SS*(10.0)**KSF(I)
KS(I)=0
15 KF(I)=0
DO 16 KLP=1,M2
DO 17 II=1,P
DO 18 I=1,P
18 PAR1(I)=PAR1(I)+OV(II,I)*ELAM(II)
CALL VARIA (PAR1,KSF,P,VAR2,N,NFT,X,Y)
VAR2=VAR2*(-1.0)**MXMN
COUNT=COUNT+1.
IF (VAR1-VAR2) 19,20,20
20 VAR1=VAR2
KS(II)=1
ELAM(II)=ELAM(II)*3.0
GO TO 21
19 DO 22 I=1,P
PAR1(I)=PAR1(I)-ELAM(II)*OV(II,I)
22 CONTINUE
ELAM(II)=ELAM(II)/(-2.0)
KF(II)=KS(II)
KS(II)=0
21 DO 23 I=1,P
CT=ELAM(I)/PAR1(I)
CTEST=ABS(CT)
IF (CTEST-1.E-08) 24,24,25
25 IF (KF(I)) 24,17,24
23 CONTINUE
GO TO 26
17 CONTINUE
16 CONTINUE
26 CONTINUE

```

C ROTATION OF AXES

C ROSEN METHOD ... (CONT'D)

CALL ROTAT(P,PAR1,PAR3,OV)

C DATA OUTPUT

C

```

      DO 27 I=1,P
      PAR1(I)=PAR1(I)/((10.)**KSF(I))
27  CONTINUE
      WRITE(6,28)KKK,(PAR1(I),I=1,P),VAR1,COUNT
28  FORMAT (' ',16X,I3,1X,10E12.5)
      DO 29 I=1,P
      PAR1(I)=PAR1(I)*((10.)**KSF(I))
29  PAR3(I)=PAR1(I)
      IF (ABS(VAR1-VAR3)-1.E-12) 30,30,31
31  VAR3=VAR1
      IF (KPN) 14,30,14
14  CONTINUE
30  IF (KPN-1) 31,32,31
31  KPN=1
      CALL TORM (P,PAR1,KSF)
      DO 33 I=1,P
33  PAR3(I)=PAR1(I)
      GO TO 34
32  DO 35 I=1,P
35  PAR1(I)=PAR1(I)/((10.)**KSF(I))
      WRITE (6,36)
36  FORMAT ('0',/,23X,'DEVIATION',6X,'CAL FUNC VALUE
* OBS FUNC VALUE
1',6X,'REACTION TIME')
      DO 37 J=1,N
      FUNC=0.

```

C FOR DATA CORRELATION, INSERT FUNCTION AFTER THIS CARD.
C

```

      GO TO (200,201,202,203) ,NFT
200  FUNC=PAR1(1)*EXP(PAR1(2)*X(J,1))+PAR1(3)*TANH(PAR1(4)
      **X(J,1))
      GO TO 210
201  CONTINUE
      GO TO 210
202  CONTINUE
      GO TO 210
203  CONTINUE
210  CONTINUE
      DEV=Y(J)-FUNC
      WRITE(6,36) DEV,FUNC,Y(J),(X(J,I),I=1,M)
36  FORMAT (' ',19X,E15.6,2X,E15.6,3X,E15.6,5X,E15.6)
37  CONTINUE
6   CONTINUE

```


C. ROSEN METHOD . . . (CONT'D)

```
WRITE (6,38) PAR1(1),PAR1(2),PAR1(3),PAR1(4),VAR1
38 FORMAT ('0',//,27X,'K1=',F8.5,2X,'K2=',F8.5,2X,'K3='
*,F8.5,2X,'K4='
1,F8.5,3X,'VARIANCE=',F10.8)
STOP
END
```


SUBROUTINE VARIA

```

SUBROUTINE VARIA (PAR1,KSF,P,VAR2,N,NFT,X,Y)
INTEGER P
DIMENSION PAR1(9),KSF(9),X(40,1),Y(40)

```

```

C   THIS SUBROUTINE CALCULATES THE VALUE OF THE FUNCTION
C   TO BE
C   OPTIMIZED. ALSO THE VARIANCE IN THE CASE OF DATA
C   CORRELATION

```

```

      DO 5 I=1,P
5  PAR1(I)=PAR1(I)/((10.）**KSF(I))
1  DEV2=0.0
      DO 2 J=1,N

```

```

C   FOR DATA CORRELATION, INSERT FUNCTION AFTER THIS CARD.

```

```

      GO TO (200,201,202,203) ,NFT
200 FUNC=PAR1(1)*EXP(PAR1(2)*X(J,1))+PAR1(3)*TANH(PAR1(4)
    **X(J,1))
      GO TO 210
201 CONTINUE
      GO TO 210
202 CONTINUE
      GO TO 210
203 CONTINUE
      GO TO 210
210 CONTINUE
      DEV2=(Y(J)-FUNC)**2+DEV2
2  CONTINUE
      VAR2=DEV2/(N-4)
      DO 3 I=1,P
3  PAR1(I)=PAR1(I)*((10.）**KSF(I))
      RETURN
      END

```


SUBROUTINE ROTAT

```

SUBROUTINE ROTAT(P,PAR1,PAR3,OV)
  INTEGER P
  DIMENSION A(9,9),B(9,9),PAR1(9),PAR3(9),OV(9,9)

C   THIS SUBROUTINE ROTATES THE AXES USING THE GRAM
C   SCHMIDT
C   ORTHOGONALIZATION PROCESS

      DO 1 I=1,P
      DO 1 J=1,P
      A(I,J)=0.0
1     B(I,J)=0.0
      DO 2 I=1,P
      DO 2 J=I,P
      A(I,J)=PAR1(J)-PAR3(J)
2     B(I,J)=A(I,J)
      SO=0.0
      DO 3 J=1,P
3     SO=SO+A(1,J)**2
      S=SO**0.5
      DO 4 J=1,P
4     OV(1,J)=A(1,J)/S
      DO 5 I=2,P
      MI=I-1
      DO 6 K=1,MI
      DOG=0.0
      DO 7 J=1,P
7     DOG=DOG+OV(K,J)*A(K,J)
      DO 8 J=1,P
8     B(I,J)=B(I,J)-DOG*OV(K,J)
6     CONTINUE
      SO=0.0
      DO 9 J=1,P
9     SO=SO+B(I,J)**2
      S=SO**0.5
      DO 10 J=1,P
10    OV(I,J)=B(I,J)/S
5     CONTINUE
      RETURN
      END

```


SUBROUTINE TORM

```
SUBROUTINE TORM (P,PAR1,KSF)
INTEGER P
DIMENSION PAR1(9),KSF(9)
```

```
C THIS SUBROUTINE MAPS THE PARAMETERS BETWEEN 0.1 & 1.0
C .
```

```
DO 1 I=1,P
1 KSF(I)=0
DO 2 I=1,P
PP1=ALOG(PAR1(I))/2.303
IF(PP1) 3,4,4
3 KSF(I)=PP1-1
GO TO 2
4 KSF(I)=PP1
2 CONTINUE
RETURN
END
```


C RUNGE - KUTTA

C RUNGE - KUTTA

```

C *****
C *
C * NUMERICAL INTEGRATION BY FOURTH ORDER *
C * RUNGE-KUTTA'S (OR RUNGE-KUTTA-SIMPSON) *
C * METHOD *
C *
C *****

```

```

C
C

```

```

      DIMENSION B(5),C(5),D(5),E(5),CA1(5),CA2(5),CA3(5)
      *,CA4(5),CA5(5),X
      1CA1(5001),XCA2(5001),XCA3(5001),XCA4(5001),XCA6(5001)
      *,T(5001),W(5)
      1,XCA5(5001),XM(5001)
      DX=0.1
      M=5
      MB=5
      READ (5,9) NFIT,II
9  FORMAT (2I5)
      DO 19 NFT=1,NFIT
      READ (5,1) CA2(1),CA3(1),CA4(1),CA5(1),UT,CA1(1)
1  FORMAT (6F10.5)
      READ (5,2) AK11,AK21,AK22,AK41
2  FORMAT (4F8.4)
      T(1)=UT
      BK11=AK11/2.
      BK22=AK22/2.
      DO 3 I=1,II
      XCA6(I)=1./(1.+AK11*T(I))
3  T(I+1)=T(I)+UT

```

C*** SET INITIAL VALUES

C

```

      DO 8 J=1,II
      I=1
7  W(I)=(-AK11*CA1(I)**2.)*UT
      E(I)=UT*(BK11*CA1(I)**2.0-(AK21+AK22)*CA2(I))
      B(I)=(AK21*CA2(I))*UT
      C(I)=(BK22*CA2(I)-AK41*CA4(I)**0.5)*UT
      D(I)=(2*AK41*CA4(I)**0.5)*UT
      IF(I-3) 4,5,15
15 IF (I-4) 4,6,6
4  CA1(I+1)=CA1(1)+0.5*W(I)
      CA2(I+1)=CA2(1)+0.5*E(I)
      CA3(I+1)=CA3(1)+0.5*B(I)
      CA4(I+1)=CA4(1)+0.5*C(I)

```


C. RUNGE - KUTTA ... (CONT'D)

```

CA5(I+1)=CA5(1)+0.5*D(I)
I=I+1
GO TO 7
5 CA1(I+1)=CA1(1)+W(I)
  CA2(I+1)=CA2(1)+E(I)
  CA3(I+1)=CA3(1)+B(I)
  CA4(I+1)=CA4(1)+C(I)
  CA5(I+1)=CA5(1)+D(I)
  I=I+1
  GO TO 7
6 XCA1(J+1)=1./6.*(W(1)+2.*W(2)+2.*W(3)+W(4))+CA1(1)
  XCA2(J+1)=1./6.*(E(1)+2.*E(2)+2.*E(3)+E(4))+CA2(1)
  XCA3(J+1)=1./6.*(B(1)+2.*B(2)+2.*B(3)+B(4))+CA3(1)
  XCA4(J+1)=1./6.*(C(1)+2.*C(2)+2.*C(3)+C(4))+CA4(1)
  XCA5(J+1)=1./6.*(D(1)+2.*D(2)+2.*D(3)+D(4))+CA5(1)

C***      RESET INITIAL VALUES
C

CA1(1)=XCA1(J+1)
CA2(1)=XCA2(J+1)
CA3(1)=XCA3(J+1)
CA4(1)=XCA4(J+1)
8 CA5(1)=XCA5(J+1)
DO 18 JJJ=1,15
  WRITE (6,10)
10 FORMAT ('1',//////////,52X,'TABLE 1',/,50X,'INPUT
  * DATA',/,50X,'---
  1-- ----')
  WRITE (6,11) AK11,AK21,AK22,AK41
11 FORMAT (' ',29X,'K11=',F4.2,5X,'K22=',F4.2,8X,'K23=
  *,F4.2,8X,'K44=
  1',F4.2,/,29X,'KK11=K11/2',19X,'KK23=K23/2')
  WRITE (6,14)
14 FORMAT (' ',45X,'INITIAL CONDITION',/,46X,'-----
  *-----',/,32
  1X,'TIME=0.0 (HR.)',14X,'INTERVAL H = 0.002',/,27X,'A10
  * =1 (MOLE/LI
  1TRE)',5X,'A2 =A3 =A4 =A5 =0.0 (MOLE/LITRE)')
  WRITE (6,16)
16 FORMAT (' ',16X,'REACTION',5X,'A1',9X,'A2',8X,'A3',8X
  *, 'A4',8X,'A5'
  1,6X,'MATERIAL*',2X,'TRUE A1**',/,16X,'TIME (HR.)',16X
  *, 'COMPONENT (
  1MOLE/LITRE)',15X,'BALNCE',3X,'MOLE/LITRE')
  DO 13 I=500,11,250
    J=I+1
    XM(J)=XCA1(J)+2*XCA2(J)+XCA3(J)*2+4*XCA4(J)+2*XCA5(J)
    T(I)=T(I)+0.0007
13 WRITE (6,12) T(I),XCA1(J),XCA2(J),XCA3(J),XCA4(J)

```


C RUNGE - KUTTA ... (CONT'D)

```
* ,XCA5(J),XM(J),XC
1A6(I)
12 FORMAT (' ',15X,F6.2,5X,5(F8.6,2X),1X,F8.6,3X,F8.6)
   WRITE (6,17)
17 FORMAT(' ',18X,'*TOTAL NUMBER OF MOLE/LITRE EQUIVALENT
   * TO A10 PRES
   LENT IN THE REACTION SYSTEM',/,19X,'AT A COMMON
   * INSTANEOUS TIME = A
   11 + 2*A2 + 2*A3 + 4*A4 + 2*A5',/,18X,'**ANALYTICAL
   * EXACT INTEGRATI
   1ON')
18 CONTINUE
19 CONTINUE
   STOP
   END
```


C PLOTTER

C PLOTTER

```

C      *****
C      *
C      * PLOTTER, EXAMPLE 1 *
C      *
C      *****

```

```

C*** THIS PROGRAM WAS WRITTEN BASED ON IBM 1627 PLOTTER
C*** MANUAL
C

```

```

      DIMENSION B(5),C(5),F(5),W(5),CA1(5),CA2(5),CA3(5)
      *,CA4(5),CA5(5),X
      1CA1(105),XCA2(105),XCA3(105),XCA4(105),XCA5(105)
      *,D(105),E(5),T(19)
      1,A1(19),A2(19),A3(19),A4(19),A5(19)
      READ (5,2) CA1(1),CA2(1),CA3(1),CA4(1),CA5(1)
      READ (5,2) AK11,AK22,AK23,AK44,AN11,AN22,AN23,AN44
2  FORMAT (8F8.6)
      NPT=101
      UT=0.1
      D(1)=UT
      DO 3 I=1,NPT
3  D(I+1)=D(I)+UT
      DO 8 J=1,NPT
      I=1
7  W(I)=(-AK11*CA1(I)**AN11)*UT
      E(I)=UT*(AK11/AN11*CA1(I)**AN11-AK22*CA2(I)**AN22-AK23
      **CA2(I)**AN2
      13)
      B(I)=UT*(AK22*CA2(I)**AN22)
      C(I)=UT*(AK23/2.*CA2(I)**AN23-AK44*CA4(I)**AN44)
      F(I)=UT*(2*AK44*CA4(I)**AN44)
      IF (I-3) 4,5,15
15 IF (I-4) 4,6,6
      4 CA1(I+1)=CA1(1)+0.5*W(I)
      CA2(I+1)=CA2(1)+0.5*E(I)
      CA3(I+1)=CA3(1)+0.5*B(I)
      CA4(I+1)=CA4(1)+0.5*C(I)
      CA5(I+1)=CA5(1)+0.5*F(I)
      I=I+1
      GO TO 7
5  CA1(I+1)=CA1(1)+W(I)
      CA2(I+1)=CA2(1)+E(I)
      CA3(I+1)=CA3(1)+B(I)
      CA4(I+1)=CA4(1)+C(I)
      CA5(I+1)=CA5(1)+F(I)
      I=I+1
      GO TO 7

```


C PLOTTER

... (CONT'D)

```

6  XCA1(J+1)=1./6.*(W(1)+2.*W(2)+2.*W(3)+W(4))+CA1(1)
   XCA2(J+1)=1./6.*(E(1)+2.*E(2)+2.*E(3)+E(4))+CA2(1)
   XCA3(J+1)=1./6.*(B(1)+2.*B(2)+2.*B(3)+B(4))+CA3(1)
   XCA4(J+1)=1./6.*(C(1)+2.*C(2)+2.*C(3)+C(4))+CA4(1)
   XCA5(J+1)=1./6.*(F(1)+2.*F(2)+2.*F(3)+F(4))+CA5(1)

C*** RESET INITIAL VALUES

   CA1(1)=XCA1(J+1)
   CA2(1)=XCA2(J+1)
   CA3(1)=XCA3(J+1)
   CA4(1)=XCA4(J+1)
8  CA5(1)=XCA5(J+1)
   DO 500 I=5,100,5
     J=I+1
500 WRITE (6,501) D(I),XCA1(J),XCA2(J),XCA3(J),XCA4(J)
     *,XCA5(J)
501 FORMAT (' ',20X,6(F10.5,2X))
     SX=0.625
     SY=9.5
     PP=5.
     PX=0.0
     PY=0.
     CALL FPLOT (1,0.,0.)
     CALL SCALF(SX,SY,PX,PY)
     CALL FGRID (0,0.,0.,PP/5.,10)
     CALL FGRID (1,0.,0.,0.05,10)
     CALL FPLOT (1,0.,0.5)
     CALL SCALF (SX,SY,0.,0.5)
     CALL FGRID (0,0.,0.5,PP/5.,10)
     CALL FPLOT (1,10.,0.5)
     CALL SCALF (SX,SY,10.,0.5)
     CALL FGRID (3,10.,0.5,0.05,10)
     CALL FPLOT (1,0.,0.)
     I=1
     J=I+1
     CALL FPLOT (2,D(I),XCA5(J))
140 Y=XCA5(J)
     CALL FPLOT (0,D(I),Y)
     IF (TEST-D(I)) 141,141,142
142 I=I+1
     J=I+1
     D(I+1)=D(I)+UT
     GO TO 140
141 CONTINUE
     CALL FPLOT (1,0.,0.)
     DO 211 I=1,19
211 READ (5,212) A1(I)
     DO 213 I=1,19
213 READ (5,212) A2(I)

```


C PLOTTER

...(CONT'D)

```

      DO 214 I=1,19
214  READ (5,212) A3(I)
      DO 215 I=1,19
215  READ (5,212) A4(I)
      DO 216 I=1,19
216  READ (5,212) A5(I)
      DO 217 I=1,19
217  READ (5,212) T(I)
212  FORMAT (F13.7)
      CALL FCHAR (4.1,-0.06,0.1,0.1,0.)
      WRITE (7,200)
200  FORMAT ('REACTION TIME (HR.)')
      CALL FCHAR (0.2,-0.0875,0.1,0.1,0.)
      WRITE (7,201)
201  FORMAT ('REACTION PATH CALCULATED FROM KINETIC MODEL
* OBTAINED FROM
1 THIS WORK')
      CALL FCHAR (2.,-0.11,0.1,0.1,0.)
      WRITE (7,202)
202  FORMAT ('HYPOTHETICAL REACTION SYSTEM, EXAMPLE NO. 1')
      CALL FCHAR (-1.3,0.175,0.1,0.1,1.57)
      WRITE (7,203)
203  FORMAT ('CONC. (MOLE/LITRE)')
      CALL FCHAR (1.2,0.39,0.08,0.08,0.)
      WRITE (7,204)
204  FORMAT ('SIMULATED EXPERIMENTAL POINTS')
      CALL FCHAR (6.8,0.46,0.08,0.08,0.)
      WRITE (7,205)
205  FORMAT ('COMPONENT')
      CALL FPOINT (-2,6.,0.41)
      CALL POINT (2)
      CALL FCHAR (7.2,0.41,0.08,0.08,0.)
      WRITE (7,207)
207  FORMAT ('A2')
      CALL FPOINT (-2,6.,0.39)
      CALL POINT (3)
      CALL FCHAR (7.2,0.39,0.08,0.08,0.)
      WRITE (7,208)
208  FORMAT ('A3')
      CALL FPOINT (-2,6.,0.37)
      CALL POINT (4)
      CALL FCHAR (7.2,0.37,0.08,0.08,0.)
      WRITE (7,209)
209  FORMAT ('A4')
      CALL FPOINT (-2,6.,0.35)
      CALL POINT (5)
      CALL FCHAR (7.2,0.35,0.08,0.08,0.)
      WRITE (7,210)
210  FORMAT ('A5')
      CALL FPOINT (1,0.,0.)

```


C . . . PLOTTER (CONT'D)

CALL EXIT
END

C LEAST SQ

C LEAST SQ

```

C *****
C *
C *
C *   LINEAR LEAST SQUARES POLYNOMIAL APPPROXIMATION *
C *
C *
C *****
C
C***  N=NO. OF INPUT DATA POINTS
C***  M=POWER OF THE POLYNOMIAL TO BE FITTED
C

```

```

      DIMENSION T(50),Y(50),SNAM(5)
      DATA SNAM/'A0 =','A1 =','A2 =','A3 =','A4 ='/
      N=19
      DO 1 I=1,N
      READ (5,2) Y(I)
1 CONTINUE
      DO 3 I=1,N
      READ(5,2) T(I)
3 CONTINUE
2 FORMAT (F13.7)
      DO 4 I=1,3
      I=I+1
      MM=M+1
      KKK=M+2
      WRITE (6,5) KKK
5 FORMAT ('1',////////,26X,'TABLE',I2)
      WRITE (6,6) M
6 FORMAT ('0',15X,'LEAST SQUARES',I2,1X,'ORDER
* POLYNOMIALS')
      CALL LEAST (T,Y,N,M,SNAM)
4 CONTINUE
      CALL EXIT
      END

```


SUBROUTINE REGEN

```
SUBROUTINE REGEN(X,Y,Z,MM,N)
  DIMENSION X(50),Y(50),Z(20)
```

```
C*** THIS SUBROUTINE REGENERATES DATA POINTS FROM THE
C*** RESULTED POLYN.
C
```

```
  WRITE(6,1)
1  FORMAT(//,29X,'REGENERATED DATA'//10X,'X MEASURED',5X
*, 'Y OBSERVED'
1,5X,'Y CALCULATED',3X,'PCT ERROR',/)
  VAR=0.
  HI=0.
  K=N
  K2=N*2
  DO 2 I=1,N
    CAL=0.
    DO 3 J=1,MM
      CAL=CAL+Z(J)*X(I)**(J-1)
3  CONTINUE
    CAT=Y(I)-CAL
    PCE=CAT/ABS(Y(I))*100.
    VAR=VAR+CAT**2
    IF (HI-ABS(PCE))4,4,2
4  HI=ABS(PCE)
2  WRITE(6,5) X(I),Y(I),CAL,PCE
5  FORMAT ( 9X,4(F11.6,4X))
  VAR=VAR/(N-MM)
  DEV=VAR**0.5
  WRITE(6,6) VAR,DEV,HI
6  FORMAT(//,10X'VARIANCE' =',F10.6//10X
*, 'STANDARD DEVIATION'
1 =',F10.6//10X, 'MAXIMUM PCT ERROR' =',F10.6)
  RETURN
  END
```


C LEAST SQ

C LEAST SQ

```

      SUBROUTINE LEAST (X,Y,N,M,SNAM)
      DIMENSION X(50),Y(50),A(50,5),P(20,20),V(20),Z(5)
      *,SNAM(5)
      NPLT=0
      DO 21 I=1,5
21  Z(I)=0.0
      MM=M+1
      DO 4 I=1,N
      DO 4 J=1,MM
4  A(I,J)=X(I)**(J-1)
      DO 5 I=1,MM
      DO 5 J=1,MM
      P(I,J)=0.
      DO 5 K=1,N
5  P(I,J)=P(I,J)+A(K,I)*A(K,J)
      DO 6 I=1,MM
      V(I)=0.
      DO 6 J=1,N
6  V(I)=V(I)+Y(J)*A(J,I)
      CALL GAUSS(P,V,MM,Z)
      WRITE(6,8)
8  FORMAT ('0',/,10X,'THE COEFFICIENTS OF THE FITTED
      * FUNCTION ARE'/)
      DO 15 I=1,MM
15 WRITE(6,7) SNAM(I),Z(I)
7  FORMAT (15X,A4,F11.8)
      CALL REGEN(X,Y,Z,MM,N)
      IF(NPLT) 9,9,14
14 CALL POLYT (X,Z,N,MM)
9  CONTINUE
      RETURN
      END

```


SUBROUTINE POLYT

```
SUBROUTINE POLYT(X,Z,N,MM)
  DIMENSION X(50),Z(20)
  WRITE(6,1)
1  FORMAT(///,32X,'PLOT TEST DATA'//25X'X CALCULATED',4X
  *, 'Y CALCULATE
  1D'//)
  XMAX=0.
  XMIN=99999.
  DO 2 I=1,N
    IF(XMAX-X(I)) 3,3,4
3  XMAX=X(I)
4  IF(X(I)-XMIN) 5,5,2
5  XMIN=X(I)
2  CONTINUE
  DELX=(XMAX-XMIN)/20.
  XY=XMIN
  DO 6 I=1,20
    CAL=0.
    DO15 J=1,MM
15  CAL=CAL+Z(J)*XY**(J-1)
    WRITE(6,7) XY,CAL
7  FORMAT(24X,2(F11.6,4X))
6  XY=XY+DELX
  RETURN
END
```


SUBROUTINE GAUSS

```

SUBROUTINE GAUSS (A,R,N,X)
DIMENSION A(20,20),R(20),X(20)

```

```

C*** THIS SUBROUTINE CALCULATES PARAMETERS OF THE POLYN.
C

```

```

      M=N-1
      DO 11 J=1,M
        S=0.
        DO 12 I=J,N
          U= ABS(A(I,J))
          IF(U-S) 12,12,112
112    S=U
      12 CONTINUE
        IF(L-J) 119,19,119
119    DO 14 I=J,N
      4    S=A(L,I)
          A(L,I)=A(J,I)
          A(1,I)=S
          S=R(L)
          R(L)=R(J)
          R(J)=S
      19 IF( ABS(A(J,J))-1.E-30) 115,115,15
115    WRITE(6,3)
      3    FORMAT (1H, 'MATRIX SINGULAR')
        RETURN
      15 MM=J+1
        DO 11 I=MM,N
          IF( ABS(A(I,J))-1.E-30) 11,111,111
111    S=A(J,J)/A(I,J)
          A(I,J)=0.0
          DO 16 K=MM,N
      16    A(I,K)=A(J,K)-S*A(I,K)
          R(I)=R(J)-S*R(I)
      11 CONTINUE
          DO 17 K=1,N
            I=N+1-K
            S=0.0
            IF(I-N) 117,17,117
117    MM=I+1
          DO 18 J=MM,N
      18    S=S+A(I,J)*X(J)
      17    X(I)=(R(I)-S)/A(I,I)
        RETURN
      END

```


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